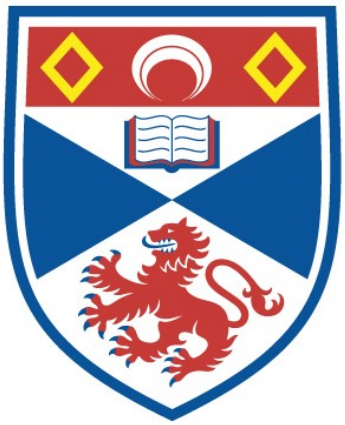
DIRECTED CHLORINATION IN SOME SUBSTITUTED ALKANES

Alan Potter

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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ABSTRACT

The work in this thesis investigates the selectivity in the direction of attack in the chlorination of a wide variety of substituted alkanes. The main chlorinating agent studied is atomic chlorine, although the selectivity of some other hydrogen abstracting radicals receives attention. Gas phase chlorination is studied, but more attention is given to the effect of solvent systems on the reaction selectivity.

The chlorination of 1,1-dichloroethane is studied. The relative Arrhenius parameters for the gas phase reaction as well as for the reaction in non-complexing and complexing liquid phase systems are determined. The reaction selectivity is shown to be a balance of enthalpy and entropy effects. The selectivity in a range of solvent systems is investigated. The novel use of perfluorinated compounds as solvents is studied and selectivities are found to be nearly as high as those in the gas phase.

Earlier work on the directive effects in the chlorination of 1-substituted butanes in the gas phase is extended to both non-complexing and complexing liquid phase media. The results agree with earlier proposals that in the liquid phase the inductive effect of a substituent influences the reactivity of the carbon centres much further along the alkane chain than in the gas phase. They also indicate that in complexing media the deactivating effect of the substituent is diminished and higher selectivities are obtained.

The chlorination and bromination of 1-nitrobutane is studied. This is one of the few studies that have been made on the halogenation of nitroalkanes. The electron withdrawing power of the nitro group makes it the strongest deactivating group so far observed.

For the first time the directive effect of two substituents, one at each end of an alkane chain, is studied. The chlorination of 1,4-disubstituted butanes are investigated. The results go some way to confirm that the polar inductive effect of a substituent is diminished in complexing media. They also confirm that in non-complexing media the effect of the substituent is felt along the whole butane chain. The gas phase results indicate that the presently held theory that in gas phase chlorination the substituent only affects the reactivity of the two carbon centres adjacent to it may not now be wholly acceptable.


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CERTIFICATE

I certify that Alan Potter, B.Sc., has spent eleven terms research work under my direction, and that he has fulfilled the conditions of the Resolution of the University Court, 1967, No.1, and as such he is qualified to submit this thesis for the degree of Doctor of Philosophy.

Professor Lord Tedder

DECLARATION

I declare that the work presented in this thesis is the result of experiments carried out by me during eleven terms in the Chemistry Department, St. Andrews University, and that it has not been previously submitted for a higher degree.

Alan Potter

ACKNOWLEDGEMENTS

I would like to thank Professor J.M. Tedder, Dr. J.C. Walton and Dr. Hari Singh of the Chemistry Department, St. Andrews, along with Dr. A. Campbell and Dr. A. Clemence of I.C.I. Mond Division for their continual help and encouragement during my research work.

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GENERAL INTRODUCTION

DIRECTED CHLORINATION IN SOME SUBSTITUTED ALKANES

General Introduction

The study of free radicals is a branch of chemistry which has grown rapidly since the turn of the century. Until fairly recently the chemistry of one electron transfer reactions was regarded as a rather obscure topic by organic chemists, this in spite of the fact that in nature they may be more common than the familiar reactions involving electron pairs. One reason may be that it is only recently that techniques have been developed to facilitate the research into these short-lived species.

In 1900, Gomberg[1] isolated the triphenyl methyl radical. Although this is a relatively long-lived species, it does represent the discovery of the first genuine free radical. Later, in 1929, Paneth and Hofeditz[2] demonstrated the existence of methyl radicals and determined their lifetime to be 10^{-3} secs at 2mm pressure. This classic experiment involved breaking down tetramethyl lead to yield methyl radicals.

$$Pb(CH_3)_4 \xrightarrow{\Delta} Pb + 4CH_3$$

These radicals combine rapidly to give ethane, but in a flow system they will react with a lead mirror downstream . By varying the distance of the lead mirror from the tetra-methyl lead upstream, the lifetime of the methyl radicals can be determined. After this, the whole field of gas phase radical reactions was opened and an extensive amount of work was carried out. In 1937, Kharasch[3], and Hey and Waters[4] independently proposed that the anti-Markovnikov addition of HBr in the liquid phase occurs by a free radical mechanism, and this led to the general acceptance of the importance of radical reactions in Organic Chemistry.

Free-radicals react in several different ways and their reactions may be classified:-

Unimolecular Reactions:-

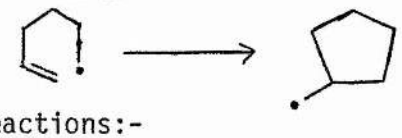
1) Radical Fragmentation

e.g. $(CH_3)_3\ CO^{\bullet} \longrightarrow CH_3^{\bullet} + (CH_3)_2CO$

2) Radical Rearrangement

e.g. $CCl_3^{\bullet}CH\ CH_2Br \longrightarrow {}^{\bullet}CCl_2\ CHCl\ CH_2Br$

3) Radical Cyclisation

e.g. 

Bimolecular Reactions:-

1) Combination

e.g. $PhCH_2^{\bullet} + {}^{\bullet}CCl_3 \longrightarrow PhCH_2CCl_3$

2) Disproportionation

E.G. $2(CH_3)_3C^{\bullet} \longrightarrow (CH_3)_3\ CH + CH_2 = C(CH_3)_2$

3) Addition

e.g. $CF_3^{\bullet} + CH_3CH = CH_2 \longrightarrow CH_3^{\bullet}CH\ CH_2CF_3$

4) Abstraction (radical transfer)

e.g. $Br^{\bullet} + CH_3CH_3 \longrightarrow CH_3CH_2^{\bullet} + HBr$

In this work we are concerned with the gas and liquid phase chlorination of organic substances by a free radical mechanism. Chlorination reactions are of considerable significance and are incorporated in several important processes in the chemical industry.[5] They are used in the manufacture of many heavy organic chemicals as well as solvents and imtermediates for plastics. The free radical chlorination of substituted alkanes occurs by a chain process including the abstraction of hydrogen. The abstracting species is usually the chlorine atom which is generated by photolysis of a chlorine molecule, but it may be a larger radical e.g. a t-butoxy radical generated by the photolysis of a t-butyl hypochlorite. The overall reaction may be represented:-

..... may be represented:-

$$RH + Cl_2 \longrightarrow RCl + HCl$$

However, this is a chain reaction which can be depicted:-

1.	$Cl_2 \xrightarrow{h\nu} 2Cl^{\bullet}$		Initiation
2.	$Cl^{\bullet} + RH \xrightarrow{k_2} R^{\bullet} + HCl$	}	Chain
3.	$R^{\bullet} + Cl_2 \xrightarrow{k_3} RCl + Cl^{\bullet}$	}	Propagation
4.	$Cl^{\bullet} + Cl^{\bullet} + M \xrightarrow{k_4} Cl_2 + M$	}	Chain Termination
5.	$R^{\bullet} + Cl^{\bullet} \xrightarrow{k_5} RCl$	}	
6.	$R^{\bullet} + R^{\bullet} \xrightarrow{k_6} R_2$	}	

(In Reaction 4., M is a third body which can be the wall of a reaction vessel or a solvent)

The sequence is initiated by the thermal or photochemical dissociation of the chlorine molecule (Reaction 1.). The chain propagation steps involve two radical transfer reactions (Reactions 2. and 3.). There are three possible termination steps (Reactions 4., 5. and 6.). The chain lengths of these reactions have been shown to be very long,[6,7] indeed quantum yields of up to 10^6 have been recorded.[8] Reaction 3. is faster than Reaction 2., so the most important termination step is Reaction 4., Reactions 5. and 6. being unimportant. So, by assuming a 'steady state' approximation and neglecting Reactions 5. and 6., the following expression can be derived:-

$$\frac{d}{dt}(R^{\bullet}) = 0 = k_2(Cl^{\bullet})(RH) - k_3(R^{\bullet})(Cl_2) \quad .....(7)$$

Similarly, an expression can be derived for the 'steady state' concentration of chlorine atoms:-

$$\frac{d(Cl^{\bullet})}{dt} = 0 = 2\emptyset I_a - k_2(Cl^{\bullet})(RH) + K_3(R^{\bullet})(Cl_2) - k_4 2(Cl^{\bullet})^2(M) \quad .....(8)$$

$\emptyset$ = the quantum yield of chlorine molecule dissociation

Ia = the amount of light absorbed

From (7) and (8):- $(Cl^{\bullet})^2 = \frac{\emptyset Ia}{k_4(M)}$

Therefore: $(Cl^{\bullet}) = \left(\frac{\emptyset Ia}{k_4(M)}\right)^{\frac{1}{2}}$ ---------- (9)

As: Rate (2) $= k_2(Cl^{\bullet})(RH)$ ---------- (10)

Substituting (9) into (10):

Rate (2) $= k_2 \left(\frac{\emptyset Ia}{k_4(M)}\right)^{\frac{1}{2}} (RH)$ ------- (11)

Equation (11) can be used to determine the absolute rate of chlorination although the determination of k_4 poses a few problems. But, if the absolute rate of one chlorination reaction is known, then the rate of another can be found by reacting the two competitively.[9] If there are two competing reactions:-

$$RH + Cl^{\bullet} \longrightarrow R^{\bullet} + HCl \quad \text{---------- (12)}$$

and $$R'H + Cl^{\bullet} \longrightarrow R'^{\bullet} + HCl \quad \text{---------- (13)}$$

we can write:-

$$-\frac{d(RH)}{dt} = k_{12}(Cl^{\bullet})(RH) \quad \text{---------- (14)}$$

and

$$-\frac{d(R'H)}{dt} = k_{13}(Cl^{\bullet})(R'H) \quad \text{---------- (15)}$$

Integrating equations (14) and (15) between the limits i and f,i.e. the initial and final concentrations, the following is obtained:-

$$\frac{k_{12}}{k_{13}} = \frac{\ln((RH)_i/(RH)_f)}{\ln((R'H)_i/(R'H)_f)} \quad \text{---------- (16)}$$

In practice, it is easier to measure product formation as opposed to the disappearance of starting materials. If conversion is kept low i.e. $(RH)_i \sim (RH)_f$ then equation (16) can be transformed to:-

$$\frac{k_{12}}{k_{13}} = \frac{k_{RH}}{k_{R'H}} = \left(\frac{(RCl)\,(R'H)_i}{(R'Cl)\,(RH)_i}\right) \quad \text{..... (17)}$$

In many chlorination reactions it is of great interest to find out the relative attack at various sites in a single molecule. In such a case:-

$(RH)_i/(R'H)_i = 1$, and so (17) simplifies to:

$$\frac{k \text{ site } 1}{k \text{ site } 2} = \frac{(\text{Product}) \text{ site } 1}{(\text{Product}) \text{ site } 2} \quad \ldots\ldots\ldots\ldots (18)$$

Thus the relative rates of hydrogen abstraction can be found directly by measuring the amount of products formed. Equations (17) and (18) are valid provided conversions are kept low (~10%) and no dichlorinated products are formed. It is also very important that the alkyl radical, $\dot{R}$, does not undergo any rearrangement reactions.

When considering the relative rates of attack at various sites in a single molecule the results are usually expressed as Relative Selectivities. This term was introduced by Hass, McBee and Weber[10] and is defined as the relative rate of abstraction per hydrogen atom i.e. if there are x hydrogens at position x in the substituted alkane molecule and y hydrogen atoms at position y, then the relative selectivity per hydrogen atom at y compared to x is RS_x^y.

$$RS_x^y = \frac{k_y}{k_x} \cdot \frac{x}{y}$$

One of the main aims of this work is to investigate the selectivity in the free radical chlorination of some substituted alkanes. The thermodynamics of the hydrogen abstraction reaction has an important bearing on the selectivity. The abstraction of hydrogen by a free radical can be represented:-

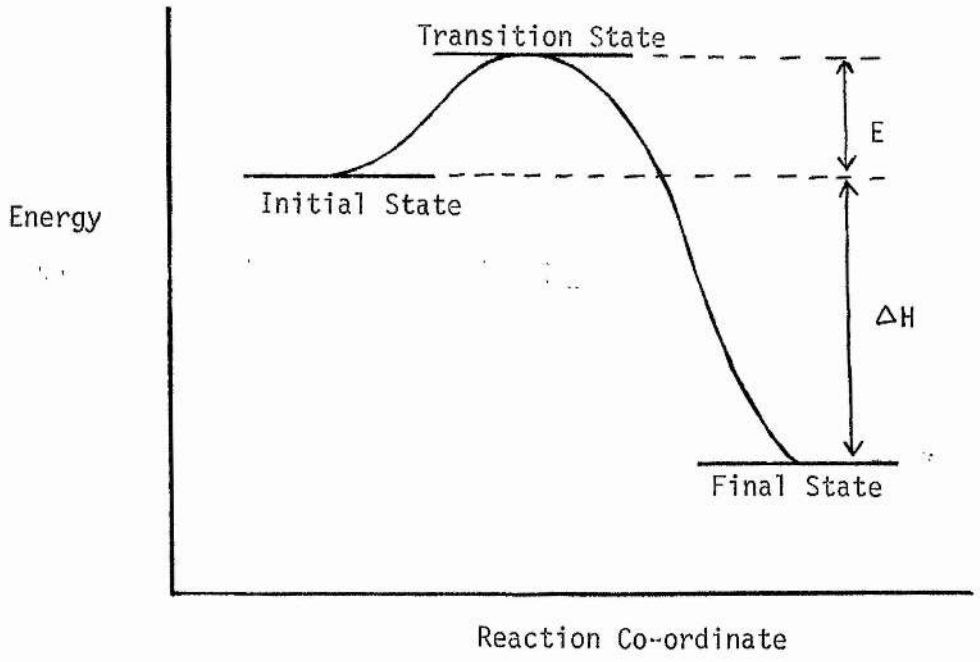
.... can be represented:-

$$X^{\bullet} + H\text{-}R \longrightarrow (X\text{----------}H\text{-------}R) \longrightarrow X\text{-}H + R^{\bullet}$$

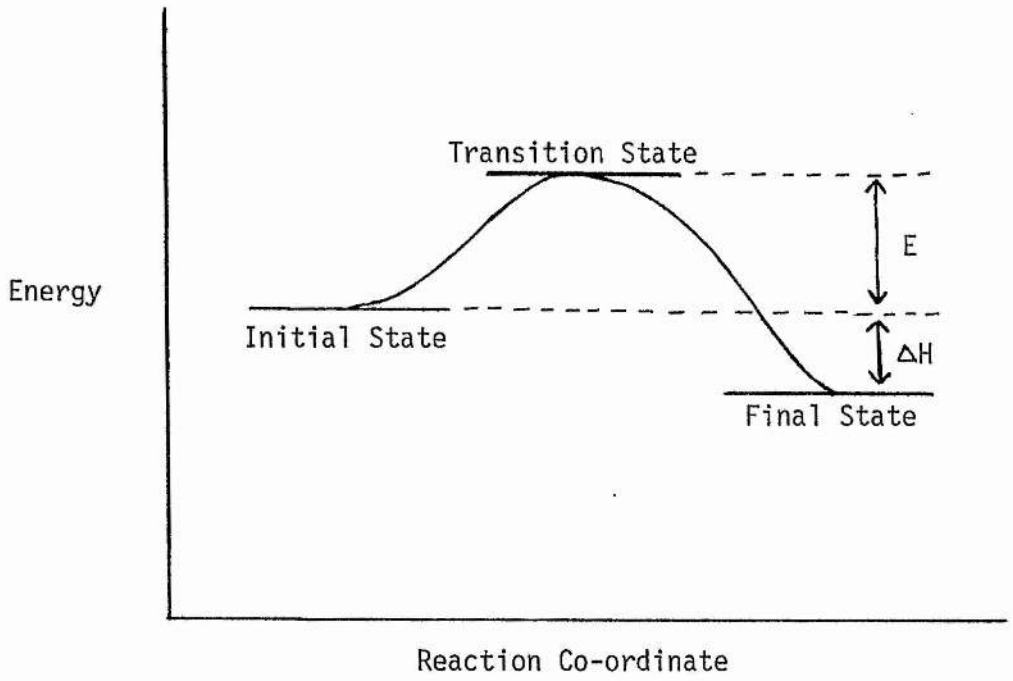
Initial State — Transition State — Final State

As the radical $X^{\bullet}$ approaches RH there is increasing electronic repulsion until there is a transition state formed at the top of a potential barrier. The reaction proceeds with repulsion between HX and the new alkyl radical, R, and there is consequently a lowering of energy. There are three types of reaction depending on the relative strengths of the bond dissociation energies of R-H and H-X. The three cases can be represented diagramatically using energy reaction co-ordinate diagrams.

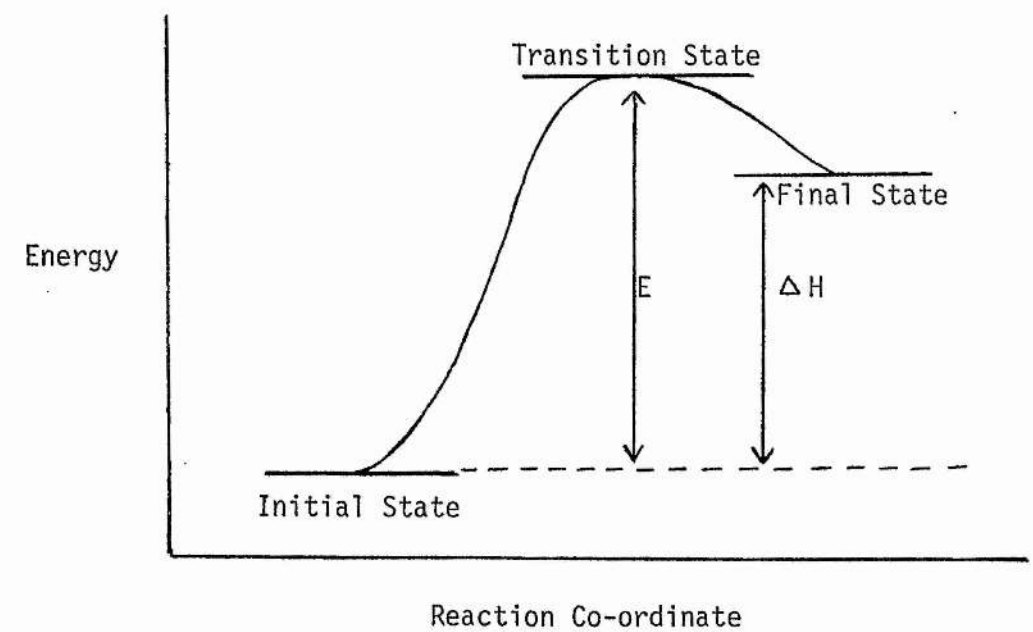
1. Exothermic Reaction: $D(H\text{-}X) > D(H\text{-}R)$



2. Thermoneutral Reaction $D(H\text{-}X) \sim D(H\text{-}R)$



3. Endothermic Reaction $D(H\text{-}X) < D(H\text{-}R)$



The atomic halogenation of alkanes and substituted alkanes provides examples of all three types of reaction. Fluorination is exothermic whilst bromination is endothermic. Atomic chlorination, with which this work is concerned, is effectively a thermoneutral reaction. From known bond dissociation energies[11] the following series can be written:-

$$CH_4 + Cl^{\bullet} \longrightarrow HCl + CH_3^{\bullet} \quad \Delta H = -1 \text{kcal mol}^{-1}$$

$$RCH_3 + Cl^{\bullet} \longrightarrow HCl + RCH_2^{\bullet} \quad \Delta H_p = -5 \text{kcal mol}^{-1}$$

$$R_2CH_2 + Cl^{\bullet} \longrightarrow HCl + R_2CH^{\bullet} \quad \Delta H_s = -9 \text{kcal mol}^{-1}$$

$$R_3CH + Cl^{\bullet} \longrightarrow HCl + R_3^{\bullet}C \quad \Delta H_t = -13 \text{kcal mol}^{-1}$$

The abstraction of hydrogen becomes increasingly exothermic on changing from primary through to tertiary hydrogens. The difference in enthalpy of abstraction of primary to tertiary hydrogens, $\Delta H_p - \Delta H_t$, is about 8kcal mol^{-1}. The difference in activation energies for the same reactions has been shown to be about 0.8kcal mol^{-1}.[9] The change in enthalpy and activation energy for a series of related reactions can sometimes be related by the Evans-Polanyi[12] equation:-

$$E = \alpha \Delta H + C$$

Therefore in the abstraction of hydrogen atoms by atomic chlorine α has a value of about 0.1. This is interpreted as meaning that the transition state has little C-H bond breaking and resembles the reactants rather than the products. The full differences in the ground state bond dissociation energies are not reflected in the transition state and consequently the reaction is not as selective as might have been predicted. This idea is in agreement with the Hammond[13] principle.

The selectivity of free radical chlorination of hydrocarbons was rationalised by Hass, McBee and Weber[10] and they proposed several chlorination rules:-

1. Carbon skeleton rearrangements do not occur during photochemical or thermal chlorinations below pyrolysis temperatures, but every possible monochloride is always formed.

2. The hydrogen atoms are always substituted at rates which are in the order: primary < secondary < tertiary.

3. At increasing temperatures, these relative rates approach 1:1:1.

4. Liquid phase chlorination gives relative rates comparable to those obtained at much higher temperature in the gas phase.

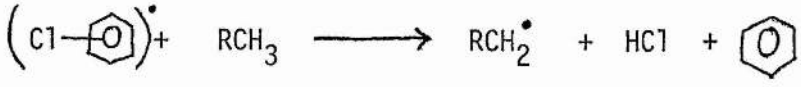
5. Moisture, carbon surfaces, and light have no effect on these ratios.

The lower selectivity of liquid phase chlorination caused some debate for many years. In fact, Russell[14] made the assumption that rate constants in gas and 'non complexing' solvent phase are the same. Walling[15] proposed a modification of the Frank-Rabinovitch 'cage' hypothesis i.e. a chlorine atom will be constrained by the surrounding solvent long enough to react even though more reactive sites are available. Later, Walling and Mayahi[16] put forward the idea that the reactants are solvated to an extent and this leads to a lowering of their energy causing the reaction to change from being slightly exothermic in the gas phase to endothermic in the liquid phase and consequently giving a change in selectivity. This idea has the drawback that it would lead to increased selectivity in the liquid phase, and this is contrary to many observations.

Tedder[17] showed that when chlorinating n-hexane the activation energy differences are greater in the liquid phase, a factor which would yield greater selectivity in the liquid phase. However, the pre-exponential factor ratios are much less in the liquid phase and taking both factors into account the selectivity in the liquid phase is much less than the gas phase. The selectivity of a chlorination reaction is governed by enthalpic and entropic effects which may even cancel each other out leading to no apparent change in selectivity in gas and liquid phase.

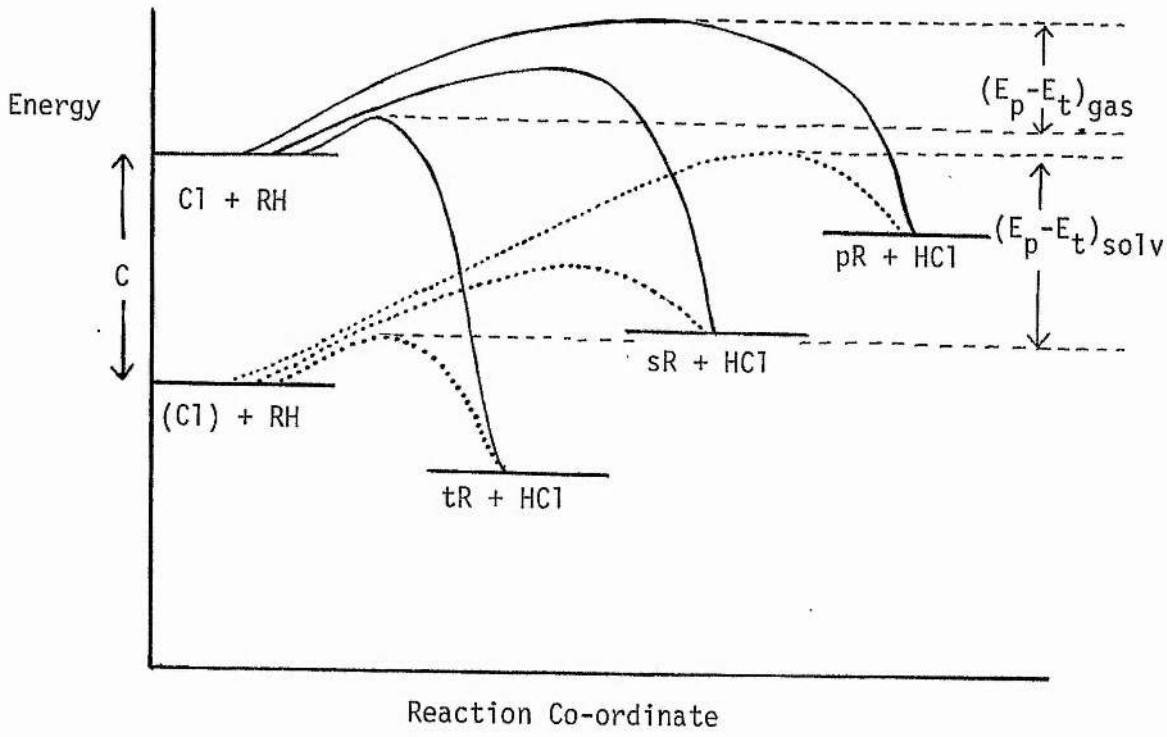
It is not a general rule that chlorination of alkanes and substituted alkanes are less selective in the liquid phase. Walling[16] and Russell[18] independently observed that if aromatic solvents are used the selectivity is markedly increased. This is attributed to a mobile equilibrium between the chlorine atom and a solvent complexed chlorine atom:-

Russell[19] proposed that benzene and the chlorine atom can form a π complex. Such species have been established[20,21] in more stable radical systems. Pulse radiolysis of dilute solutions of a series of aromatic hydrocarbons in carbon tetrachloride has allowed the observation of transient spectra ($t_{\frac{1}{2}} \sim 10^{-6}$sec) which have been assigned to a charge transfer complex between the chlorine atom and the aromatic solvent[22]. It is proposed that the abstraction of a primary hydrogen in an aromatic solvent will proceed:-



$$\Delta H = (-5 + C) \text{ kcal/mol}$$

C is the stabilising energy gained by forming the complex. This causes the abstraction of primary, secondary and tertiary hydrogens to become increasingly endothermic resulting in greater activation energies. Walling[16] represented the situation schematically:-



The differences in activation energy between primary, secondary and tertiary hydrogen abstraction reactions become greater in the liquid phase when a complexing solvent is present e.g. $(E_p-E_t)_{GAS} < (E_p-E_t)_{SOLV}$.

All solvents probably solvate the reactants but 'complexing' solvents have a much greater stabilising energy, C, which leads to larger differences in activation energy and hence to greater selectivity.

The introduction of a substituent into a hydrocarbon chain has a tremendous effect on the distribution of chlorinated products compared to the unsubstituted hydrocarbon in both gas and liquid phase reactions. In this work the effect of substituent which do not encourage competition from polar reactions will be considered e.g. carboxylic acids, acid chlorides, esters and nitriles. Substituents such as ketone groups encourage chlorination α to it because of polar addition of enolic forms.

When a free radical, $X^{\bullet}$, attacks the chain in a substituted alkane, two effects which have a bearing on the reactivity are:-

1. The strength of the C-H bond being broken
2. The repulsive polar or inductive effect i.e. the electrostatic repulsion between the incipient products of the reaction caused by charge-charge and dipole-dipole repulsions e.g.

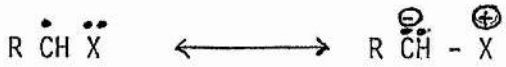
These repulsions have the effect of increasing the activation energy.

When the attacking species is a chlorine atom, $Cl^{\bullet}$, the transition state resembles the reactants more closely than the products, and so the bond dissociation energy plays little part in determining the reactivity.

The repulsive polar effect is much more important, and when the substituent is electron withdrawing it leads to the deactivation of the carbon atoms α and β to it. Singh and Tedder[23] observed that in gas phase chlorination deactivation is only significant at carbons α and β to the substituent but in the liquid phase the inductive effect is present right along the carbon chain.

This has been attributed to the solvent facilitating charge separation in the transition state.

Whereas the reactivity of the β position to a substituent is controlled mainly by the repulsive polar effect the reactivity of the α position has another effect to be considered. The stability of the α radical can be increased by means of resonance stabilization:-



This can be shown in terms of molecular orbitals:-

σ or trigonal radical π or planar radical

The reactivity at the α position during the chlorination of a substituted alkane is a compromise between the activating resonance stabilization effect and the deactivating repulsive polar effect.

The aim of this work is to add more data to our knowledge of selectivity in free radical chlorination of substituted alkanes and particularly to investigate the effect of solvents on selectivity. The work is divided into four parts. In Part I a reasonably extensive investigation into the gas and liquid phase chlorination of 1,1-dichloroethane is carried out. This was done in conjunction with I.C.I. Mond Division and the aim was to investigate conditions when the reaction selectivity would be changed and explain why. Part II continues the work of Tedder et al on the chlorination of substituted butanes. In particular, the work is extended to the liquid phase in both 'complexing' and 'non-complexing' solvents. Part III extends the work still further by investigating the photochlorination of 1,4 disubstituted butanes and observing how the inductive effects of two substituents compete with one another. In Part IV the gas and liquid phase halogenation of 1-nitrobutane is investigated.

PART ONE

The Photochlorination of 1,1-Dichloroethane

Part One

The Photochlorination of 1,1-Dichloroethane

Introduction

This work was undertaken as a co-operative assignment with I.C.I. Mond Division as part of an S.R.C. Case Award. The main reason for studying the chlorination of 1,1-dichloroethane is the commercial importance of the reaction. The two products are 1,1,1-trichloroethane and 1,1,2-trichloroethane. The valuable product is 1,1,1-trichloroethane, it is used primarily as an organic solvent and for cleaning metal surfaces in machines. It is rapidly replacing other chlorinated solvents e.g. tetrachloroethylene, because of its lower toxicity. The other product, 1,1,2-trichloroethane has no real industrial applications. The selectivity of the reaction, and the factors which control it, have important applications to the chemical industry.

Hydrogen abstraction from halogenated ethanes has been studied for fluorination,[24,25] chlorination and bromination.[26] Migita et al[27] investigated the gas phase photochlorination of the range of chloroethanes and determined their relative reactivities. By plotting log (reactive reactivity) of the C-H bond versus Taft's substituent constants for the series:-

CH_3R, CH_2ClR, and $CHCl_2R$ where R can be:-
$-CH_3$, $-CH_2Cl$, $-CHCl_2$ or $-CCl_3$, it was determined that the principal factor governing reactivities is due to the inductive effect of the substituents. There is enhanced reactivity of the α positions due to resonance stabilization and this surpasses the deactivating inductive effect in the series:-

$$H - CH_2CCl_3 < H - CHCl\ CCl_3 < H - CCl_2CCl_3$$

Martens et al[28] measured the Arrhenius parameters for the chlorination of the range of chloroethanes in the gas phase. This work was later extended to liquid phase chlorination in complexing and non-complexing media.[29,30] They concluded that the change in selectivity on passing from gas to liquid phase is due mainly to the decreased activation energy for primary and secondary hydrogen abstractions.

The aim of this part of the work is to study the effect of changing reaction conditions on the selectivity of the chlorination of 1,1-dichloroethane. Some of Marten's work is repeated essentially to try and obtain more accurate Arrhenius parameters, especially in liquid phase reactions. The effect of various solvent systems is investigated to find out the effect, if any, of solvent polarity and viscosity. The effect of benzene and perdeuterobenzene as a solvent over a solvent/substrate concentration range is studied. As well as using molecular chlorine, t-butyl hypochlorite and sulphuryl chloride are used as chlorinating agents. Finally the effect of complexing solvents on the reaction of 1,1,2-trichloroethane is investigated.

Experimental

Materials

The chlorine used in the experiments in the liquid phase was obtained directly from a cylinder supplied by British Oxygen Co. In the gas phase it was purified by trap to trap distillation before being stored in a large storage bulb. The 1,1-dichloroethane (B.D.H.) was purified by distillation on a Buchii spinning band column and the purity checked by gas-liquid chromatography. Samples of essentially 100% purity can be obtained by this method. Similarly the 1,1,2-trichloroethane (Ralph H. Emanuel) was purified on a spinning band column.

All the solvents were used as supplied by the manufacturer. The sulphuryl chloride (Hopkins and Williams) was used as supplied and the t-butyl hypochlorite was synthesised as follows:-

Preparation of t-butyl hypochlorite

The t-butyl hypochlorite was prepared by the method described by Stoddart.[31] Into an excess of sodium hypochlorite solution at below $0^{o}C$ t-butanol was added, and the reaction mixture constantly stirred. After about an hour, the t-butyl hypochlorite separated out as a yellow oily liquid.

$$tBuOH + NaOCl \longrightarrow tBuOCl + NaOH$$

The yellow oil was separated off and passed down a column containing sodium hydroxide pellets. This was to remove any chlorine which might be present and affect the results of the selectivity of t-butyl hypochlorite. It was then dried with calcium chloride and stored in the dark in a darkened bottle. The purity was checked by g.l.c. analysis and only traces of impurity were present.

Repurification was not necessary provided it was used within 2 - 3 weeks.

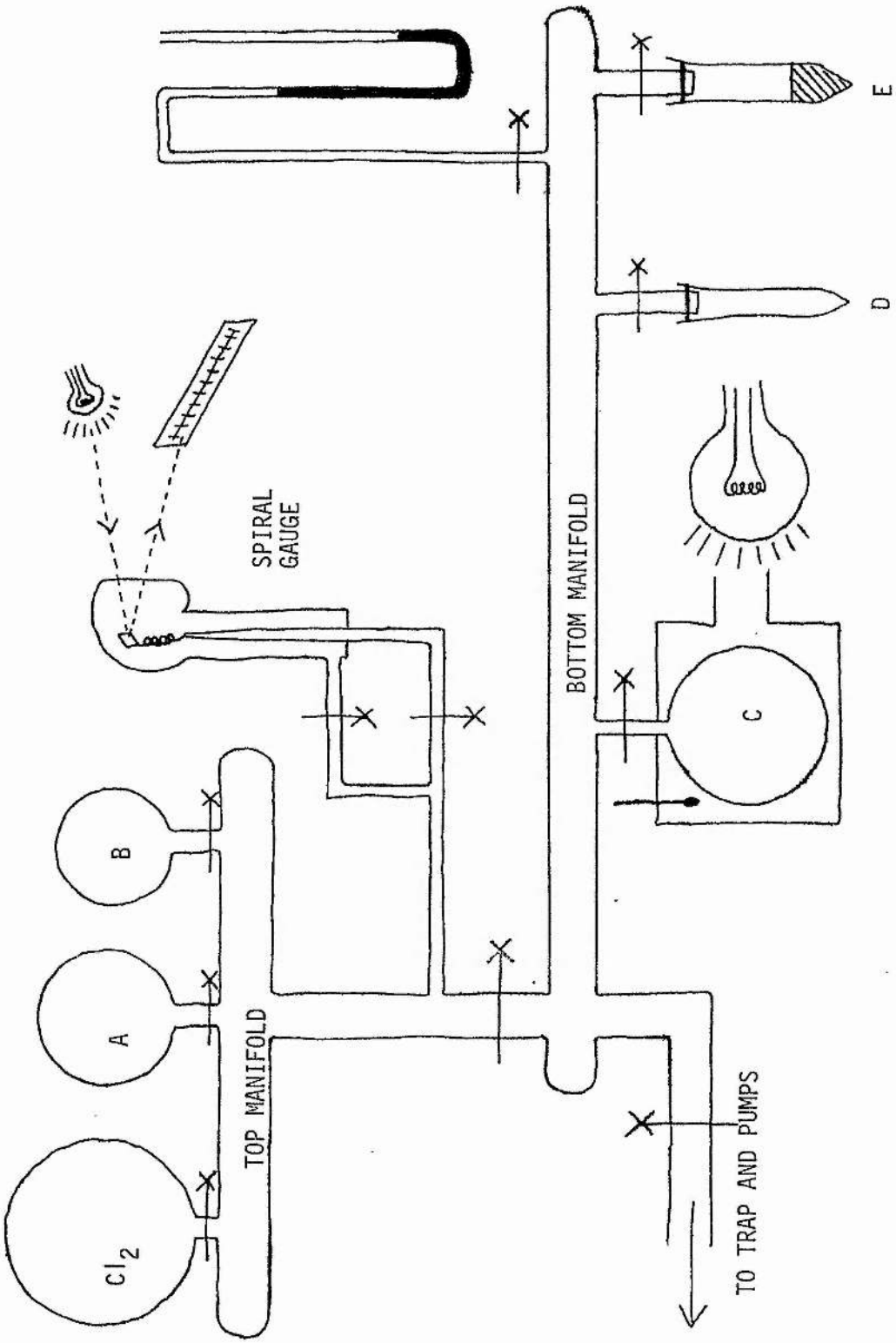
Apparatus and Procedure

Gas Phase Reactions: The experiments in the gas phase were carried out in a static system on the vacuum line illustrated in Fig.1. The line consisted of two manifolds, pressure being measured by both a mercury manometer and a calibrated gas spiral gauge. The reaction vessel, C, the product collection tube, D, and the starting material container, E, were all attached to the bottom manifold. To the top manifold was attached the chlorine storage bulb as well as two bulbs of known volume, A and B. The volume of the system was calibrated by allowing air into the line from a vessel of known volume and pressure. From the change in pressure as the air entered the various sections of the line the volume of these sections could be calculated from the gas laws. All the taps on the line were the Jencons greaseless variety and consequently did not need to be degassed.

The vacuum was maintained by a mercury diffusion pump backed by a rotary oil pump. To avoid the chlorine reacting with the mercury in the manometer its pressure was measured on the glass spiral gauge.

Reaction conditions were arranged so that there were ten parts 1,1-dichloroethane to one part chlorine. The bottom manifold was sealed and the reaction vessel left open. The starting material was allowed to diffuse into the manifold and reaction vessel from E until there was a pressure of 100mm Hg and tap E closed. The reaction vessel was then sealed and the excess 1,1-dichloroethane in the manifold condensed back into E. The reactant in the reaction vessel was then condensed down using a Dewar flask containing liquid nitrogen.

FIGURE I



VOLUMES: A = 337cm^3 B = 133cm^3 C = 331cm^3

TOP MANIFOLD = 399cm^3 BOTTOM MANIFOLD = 632cm^3

Similarly, the top manifold was sealed then bulb A opened. Chlorine diffused into the manifold after its storage bulb was opened and the pressure, monitored on the calibrated gas spiral gauge, was allowed to reach 10mm before the storage bulb was closed again. Bulb A was then sealed off and the excess chlorine condensed back into the storage bulb. Once the excess reactants had been condensed back into their storage vessels and resealed the top and bottom manifolds were opened up and the chlorine in A distilled through to the reaction vessel C. The reaction vessel was then resealed as soon as all the chlorine had distilled through, about ten minutes being allowed for this.

Meantime, an oven with a sliding shutter attachment had been heated up to the required temperature. The reaction vessel was then immersed in the oven and the system kept in the dark until, after about fifteen minutes, thermal equilibrium was reached. The shutter was then opened exposing the vessel to the radiation from a 150W lamp. Depending on temperature, the vessel was irradiated from thirty minutes to two hours. The reaction mixture was then distilled over into a collecting tube, D, attached to the bottom manifold. At least half-an-hour was allowed for the higher boiling products to condense. At all times, the vacuum in the line was monitored by a high frequency tesla coil.

Liquid Phase Reactions: The reactions in liquid phase were carried out in round bottomed flasks of known volume as illustrated in Figure 2. The vessel was always filled to the brim with reactants in order to minimise any possibility of gas phase reactions. A stopper with a long capillary tube attached was put in the top of the flask to allow the HCl produced to escape. Again to minimise the possibility of gas phase reactions the capillary tube and the top of the flask was blacked out. In the cases where a solvent was used, a known volume was saturated with chlorine before a known volume of 1,1-dichloroethane was added. The whole apparatus was then shaken to ensure adequate mixing.

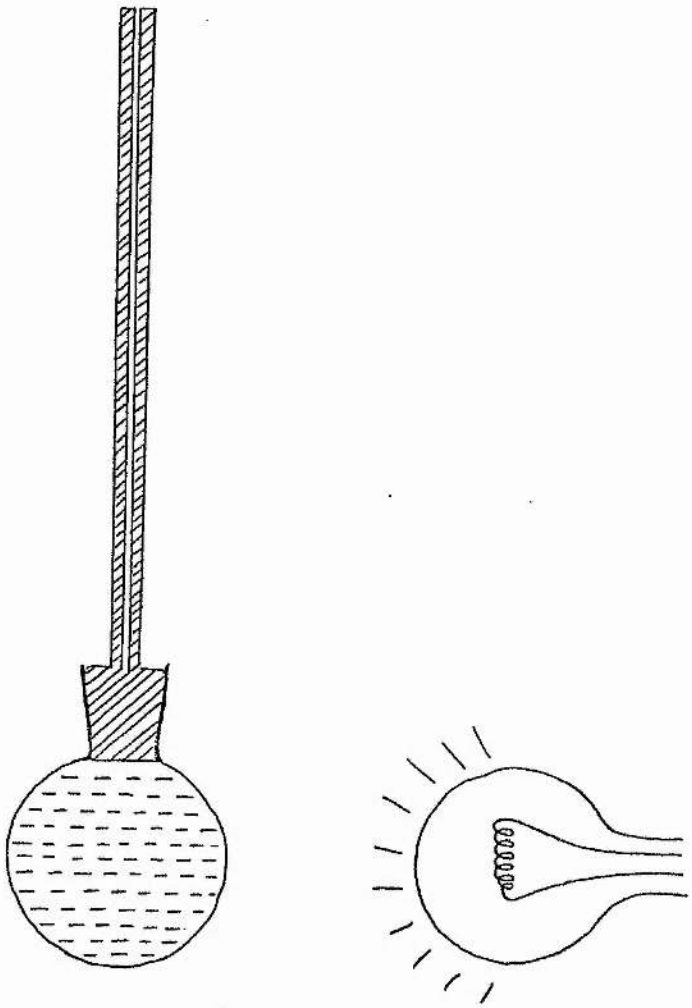
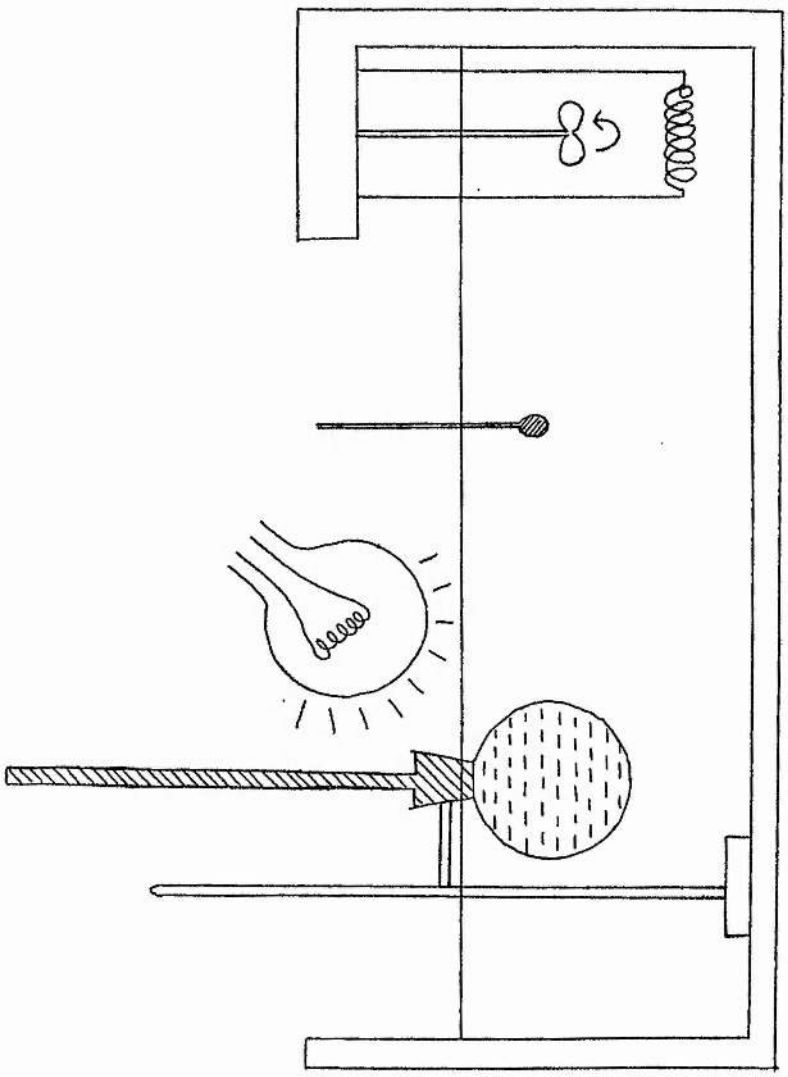


FIGURE 2

FIGURE 3



The reaction mixture was irradiated with light from a 150W lamp. The irradiation time varied but the end of the reaction was noted when the mixture appeared colourless, indicating all the chlorine had reacted.

When the liquid phase reaction was studied over a temperature range, the apparatus illustrated in Figure 3 was used. The temperature was kept constant by a thermostat in the water bath. In these reactions, the 1,1-dichloroethane and solvent were mixed beforehand thenthe flask immersed in the bath for fifteen minutes to reach thermal equilibrium. The chlorine gas was then bubbled into the reaction flask directly from the cylinder. The capillary tube was replaced and the mixture irradiated with a 150W lamp until the reaction was complete.

For the reaction using sulphuryl chloride visible light was found to be insufficient to break the S-Cl bond and so ultraviolet light was used. The apparatus used is illustrated in Figure 4. U.V. light was provided by a medium pressure mercury lamp and the heating effect was minimised by a cooling jacket of water. The reactants were mixed by means of a magnetic stirrer. The temperature of the reactants was about room temperature, and the irradiation time was two hours.

Analysis of the Products

The reaction products of both gas and liquid phase reactions were analysed by gas liquid chromatography. The column was a 12' glass column packed with a 15% silicone oil stationary phase on 100/120 mesh 'Celite". Injections were made using a 10ml Hamilton syringe. The oven temperature of 120^{o}C was maintained by a thermostatically controlled oven.

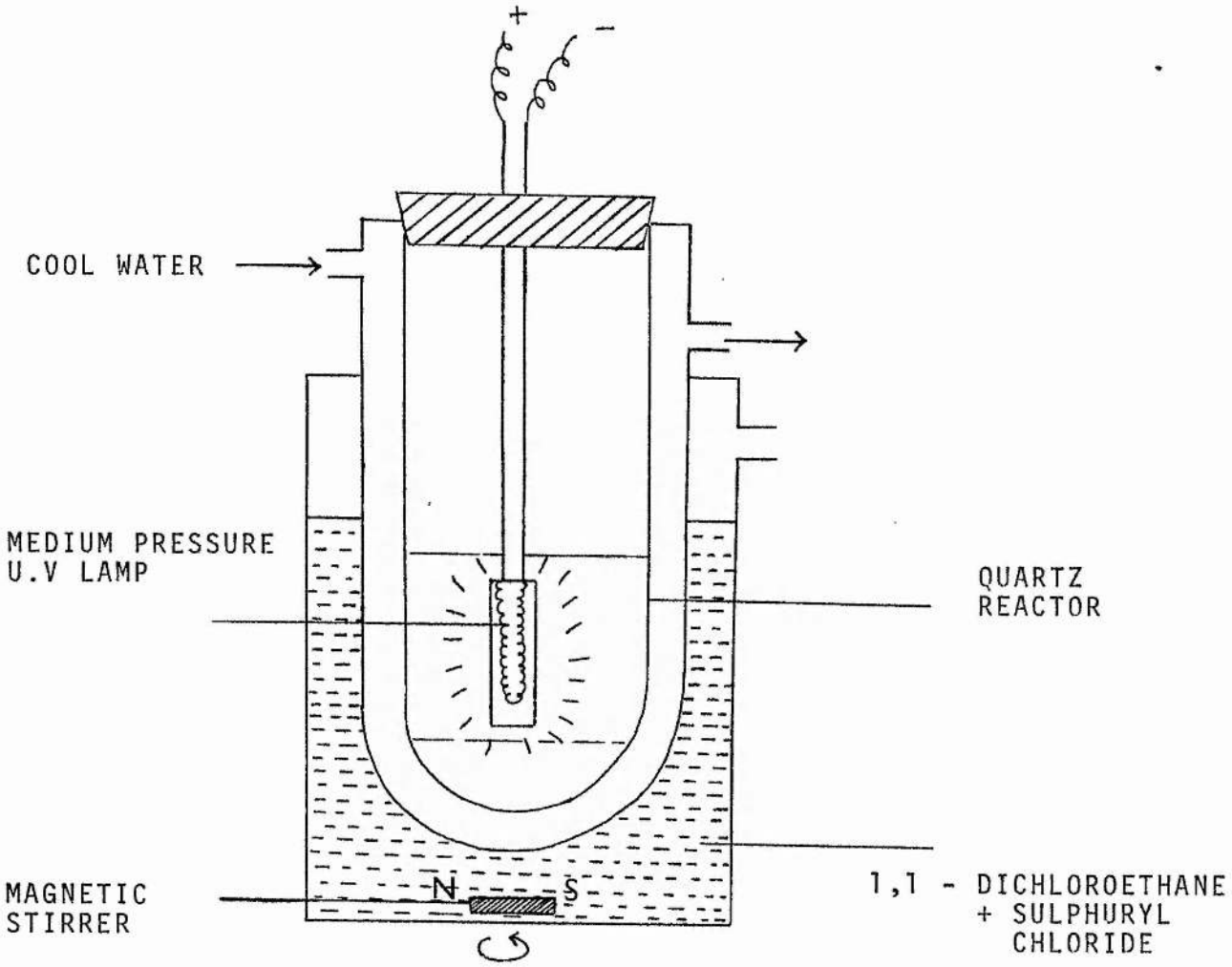

+
−
COOL WATER
MEDIUM PRESSURE
U.V LAMP
QUARTZ
REACTOR
MAGNETIC
STIRRER
N
S
1,1 - DICHLOROETHANE
+ SULPHURYL
CHLORIDE

FIGURE 4

The detector was a Griffin and George D6 gas density balance. This system is an analogue of the Wheatstone bridge; the two legs of the balance being the analogues of the resistances and a sensitive anemometer being the analogue of the ammeter. There were two flows of carrier gas, one through the column and one as a reference. When the two flows were the same there was no flow through the anemometer. When a sample was eluted from the column the difference in densities of the two gases caused the rate of flow through the anemometer to be proportional to the difference in densities. The amplified electrical response was recorded on a HoneywellBrown 1 millivolt recorder and a chromatogram was produced.

When a weight q of a sample of molecular weight M passes through the density balance in a stream of carrier gas molecular weight m, then the measured peak area A on the chromatogram is given by:-

$$q = k A \frac{M}{(M-m)}$$

k is a constant for the instrument. Therefore the concentration of the sample is given by:-

$$\frac{q}{M} = k \frac{A}{(M-m)}$$

So the relative amounts of products are directly proportional to the peak areas, and the system does not require calibration. The areas were measured using a fixed arm planimeter.

Identification of Products

In the chlorination of 1,1-dichloroethane there are only two products: 1,1,1-trichloroethane and 1,1,2-trichloroethane. Their identity was established by injecting authentic samples into the g.l.c. machine and finding their retention times. Thus their position in the reaction mixture analysis was established.

Analysis of Results

Because the relative amounts of reaction products are determined directly from g.l.c. analysis, there is a direct measure of the relative rate constants for the hydrogen abstraction reactions. We have established that:-

$$\frac{k_{\text{site 1}}}{k_{\text{site 2}}} = \frac{(\text{Product})_{\text{site 1}}}{(\text{Product})_{\text{site 2}}} \qquad (18)$$

Thus $^{kt}/kp$ was determined along with the relative selectivity RS_p^t, i.e. the reactivity per hydrogen atom.

When the reaction was carried out over a temperature range, the data was processed to yield the Arrhenius parameters; i.e. the differences in activation energy between the primary and tertiary hydrogen abstraction steps and the ratio of the pre-exponential factors. From the Arrhenius equation:-

$$\ln \left(\frac{k_t}{k_p}\right) = \ln \left(\frac{A_t}{A_p}\right) - \frac{(E_t - E_p)}{RT}$$

So a plot of $\ln (^{k}t/k_p)$ versus $^{1}/T$ gives:-

Slope $\dfrac{E_p - E_t}{R}$

Intercept $\ln \left(\dfrac{A_t}{A_p}\right)$

From which $(E_p - E_t)$ and $^{A}t/A_p$ may be determined.

RESULTS

Gas Phase Photochlorination of 1,1-Dichloroethane

G.L.C. column: 12' 15% Silicone Oil on Celite
Oven Temperature 120°C

Reaction Temperature: 23°C

	CH_3 ———	$CHCl_2$
% Distribution	5.78	93.02
	6.74	91.59
	6.69	92.15
	7.22	90.75
	7.26	90.17
Mean:	$6.74(\pm 0.60)$	$91.74(\pm 0.89)$

$\frac{kt}{kp} = 13.72(\pm 1.44)$; $RS_p^t = 41.15(\pm 4.33)$

Reaction Temperature: 30 - 32°C

	CH_3 ———	$CHCl_2$
% Distribution	8.64	87.29
	9.21	84.46
	10.79	84.50
Mean:	$9.55(\pm 1.11)$	$85.41(\pm 1.62)$

$\frac{kt}{kp} = 9.03(\pm 1.14)$; $RS_p^t = 27.10(\pm 3.43)$

Reaction Temperature: 53 - 56°C

	CH_3 ———	$CHCl_2$
% Distribution	9.15	90.85
	11.10	88.90
Mean:	$10.12(\pm 1.38)$	$89.80(\pm 1.32)$

$\frac{kt}{kp} = 8.97(\pm 1.36)$; $RS_p^t = 26.91(\pm 4.07)$

Reaction Temperature: 85 - 90°C

% Distribution	CH_3	$CHCl_2$
	13.10	86.90
	14.12	85.88
	12.02	87.98
Mean:	13.08($\pm$1.05)	86.92($\pm$1.05)

$\frac{kt}{kp}$ = 6.68($\pm$0.62); RS_p^t = 20.03($\pm$1.86)

Reaction Temperature: 102 - 110°C

% Distribution	CH_3	$CHCl_2$
	13.06	86.94
	12.12	87.88
	15.14	84.86
Mean:	13.44($\pm$1.55)	86.56($\pm$1.55)

$\frac{kt}{kp}$ = 6.50($\pm$0.83); RS_p^t = 19.51($\pm$2.50)

Reaction Temperature: 126 - 136°C

% Distribution	CH_3	$CHCl_2$
	15.64	84.36
	14.87	85.13
	16.01	83.99
Mean:	15.51($\pm$0.58)	84.49($\pm$0.58)

$\frac{kt}{kp}$ = 5.45($\pm$0.58); RS_p^t = 16.36($\pm$0.74)

Reaction Temperature: 185 - 195°C

% Distribution	CH_3	$CHCl_2$
	14.00	86.00
	17.32	82.68
	17.45	82.55
	14.33	85.67
	14.26	85.74
Mean:	15.47($\pm$1.75)	84.53($\pm$1.75)

$\frac{kt}{kp}$ = 5.52($\pm$0.71); RS_p^t = 16.56($\pm$2.13)

Reaction Temperature: 230 - 240°C

% Distribution	CH_3	$CHCl_2$
	15.45	84.55
	14.12	85.88
	16.61	83.39
	21.26	78.74
	14.62	85.37
Mean:	16.41($\pm$2.87)	83.59($\pm$2.87)

$\frac{kt}{kp} = 5.22(\pm 0.94)$; $RS_p^t = 15.67(\pm 2.82)$

Summarising these results in order to obtain Arrhenius parameters:-

T^oK	$10^3/T$	kt/kp	$\ln(kt/kp)$
296	3.38	13.72	2.62
304	3.29	9.03	2.20
328	3.05	8.97	2.19
361	2.77	6.68	1.90
379	2.64	6.50	1.87
404	2.48	5.45	1.70
463	2.16	5.52	1.71
508	1.97	5.22	1.65

Plot of $\ln(kt/kp)$ vs. $1/T$ gives:-

$$E_p - E_t = 1{,}194(\pm 216) \text{ cal/mol}$$
$$\ln \frac{(A_t)}{(A_p)} = 0.349(\pm 0.299)$$

Neat Liquid Phase Photochlorination of 1,1-Dichloroethane

G.L.C. column: 12' 15% Silicone Oil on Celite
Oven Temperature 120°C

Reaction Temperature: 0.5°C

% Distribution	CH_3	$CHCl_2$
	25.21	74.79
	26.04	73.95
	23.38	76.62
	23.80	76.20
Mean:	24.61($\pm$1.23)	75.39($\pm$1.23)

$\frac{kt}{kp}$ = 3.06 ($\pm$0.2) RS_p^t = 9.18 ($\pm$0.61)

Reaction Temperature: 3 - 5°C

% Distribution	CH_3	$CHCl_2$
	24.33	75.67
	25.30	74.70
	24.93	75.07
	24.85	75.15
	25.18	74.88
Mean:	24.92($\pm$0.38)	75.08($\pm$0.38)

$\frac{kt}{kp}$ = 3.01 ($\pm$0.06) RS_p^t = 9.04 ($\pm$0.18)

Reaction Temperature: 12 - 14°C

% Distribution	CH_3	$CHCl_2$
	25.64	74.36
	26.92	73.08
	25.28	74.72
	26.67	73.33
Mean:	26.13($\pm$0.79)	73.86($\pm$0.79)

$\frac{kt}{kp}$ = 2.83 ($\pm$0.12) RS_p^t = 8.48 ($\pm$0.35)

Reaction Temperature: 19 - 21°C

% Distribution	CH_3	$CHCl_2$
	25.57	74.43
	25.65	74.35
	26.77	72.23
	29.07	70.93
	26.94	73.06
Mean:	26.80($\pm$1.41)	73.20($\pm$1.41)

$\frac{kt}{kp}$ = 2.73 ($\pm$0.19) RS_p^t = 8.22 ($\pm$0.57)

Reaction Temperature: 27°C

% Distribution	CH_3	$CHCl_2$
	25.85	74.15
	25.53	74.47
	25.96	74.04
	24.16	75.84
Mean:	25.38($\pm$0.83)	74.62($\pm$0.83)

$\frac{kt}{kp}$ = 2.94 ($\pm$0.13) RS_p^t = 8.82 ($\pm$0.40)

Reaction Temperature: 33°C

% Distribution	CH_3	$CHCl_2$
	26.60	73.40
	26.68	73.32
	25.87	74.13
	27.01	72.99
	27.91	72.09
Mean:	26.81($\pm$0.74)	73.19($\pm$0.74)

$\frac{kt}{kp}$ = 2.73 ($\pm$0.10) RS_p^t = 8.19 ($\pm$0.31)

Reaction Temperature: 37.5 - 38.5°C

% Distribution	CH_3	$CHCl_2$
	25.27	74.73
	28.60	71.40
	26.07	73.93
	27.81	72.19
Mean:	26.94($\pm$1.53)	73.06($\pm$1.53)

$\frac{kt}{kp}$ = 2.71 ($\pm$0.21) RS_p^t = 8.16 ($\pm$0.64)

Reaction Temperature: 42°C

% Distribution	CH_3	$CHCl_2$
	26.88	73.12
	29.32	70.68
	27.62	72.38
	27.67	72.33
Mean	27.87($\pm$1.03)	72.13($\pm$1.03)

$\frac{kt}{kp}$ = 2.59 ($\pm$0.13) RS_p^t = 7.76 ($\pm$0.39)

Reaction Temperature: 48°C

% Distribution	CH_3	$CHCl_2$
	33.33	66.67
	32.05	67.95
	31.59	68.41
	28.95	71.05
	28.30	71.40
Mean:	30.84($\pm$2.14)	69.16($\pm$2.14)

$\frac{kt}{kp}$ = 2.24 ($\pm$0.23) RS_p^t = 6.72 ($\pm$ 0.68)

Reaction Temperature: 53.5 - 54.5°C

% Distribution	CH_3	$CHCl_2$
	29.86	70.14
	31.17	68.83
	30.93	69.07
	31.72	68.28
	29.71	70.29
Mean:	30.68($\pm$0.87)	69.32($\pm$0.87)

$\frac{kt}{kp}$ = 2.26($\pm$0.09) RS_p^t = 6.78($\pm$0.28)

T(K)	$10^3/T(K^{-1})$	kt/kp	$\ln(kt/kp)$
273.5	3.66	3.06	1.12
277	3.61	3.01	1.10
286	3.49	2.83	1.04
293	3.41	2.73	1.00
300	3.33	2.94	1.08
306	3.27	2.73	1.00
311	3.22	2.71	0.99
315	3.17	2.59	0.95
321	3.12	2.24	0.81
327	3.06	2.26	0.82

Plot $\ln(kt/kp)$ $^1/T$ gives:-

$$E_p - E_t = 910\ (\pm 177)\ \text{cal mol}^{-1}$$

$$\ln \frac{(At)}{(Ap)} = -0.534(\pm 0.297)$$

Liquid Phase Photochlorination of 1,1-Dichloroethane in Benzene

G.L.C. Column: 12' 15% Silicone Oil on Celite
Oven Temperature 120°C

$\frac{(SOLVENT)}{(SUBSTRATE)} = 3.79$

Reaction Temperature: 0.5°C

% Distribution	CH_3	$CHCl_2$
	8.58	91.42
	8.39	91.61
	9.48	90.52
	6.85	93.15
	10.70	89.30
Mean:	8.80($\pm$1.42)	91.20($\pm$5.86)

$\frac{kt}{kp} = 10.61(\pm 1.95)$ $RS_p^t = (\pm 5.86)$

Reaction Temperature: 11 - 13°C

% Distribution	CH_3	$CHCl_2$
	7.69	92.31
	10.11	89.89
	8.48	91.52
	12.78	87.22
Mean:	9.77($\pm$2.25)	90.23($\pm$2.25)

$\frac{kt}{kp} = 9.63(\pm 2.27)$ $RS_p^t = 28.88(\pm 6.80)$

Reaction Temperature: 22.5 - 25.5°C

% Distribution	CH_3	$CHCl_2$
	8.44	91.56
	13.79	86.21
	8.64	91.36
	8.72	91.28
	13.45	86.55
Mean:	10.61($\pm$2.75)	89.39($\pm$2.75)

$\frac{kt}{kp}$ = 8.68($\pm$2.70) RS_p^t = 26.04($\pm$8.09)

Reaction Temperature: 34°C

% Distribution	CH_3	$CHCl_2$
	10.29	89.71
	10.74	89.26
	10.18	89.82
	12.05	87.95
	12.20	87.80
Mean:	11.09($\pm$0.97)	88.91($\pm$0.97)

$\frac{kt}{kp}$ = 8.07($\pm$0.78) RS_p^t = 24.21($\pm$2.33)

Reaction Temperature: 44°C

% Distribution	CH_3	$CHCl_2$
	12.68	87.32
	12.65	87.35
	14.45	85.55
	14.49	85.51
	13.98	86.02
Mean:	13.65($\pm$0.92)	86.35($\pm$0.92)

$\frac{kt}{kp}$ = 6.35($\pm$0.51) RS_p^t = 19.06($\pm$1.52)

Reaction Temperature: 55°C

% Distribution	CH_3	$CHCl_2$
	15.76	84.24
	14.96	85.04
	16.07	83.93
	15.06	84.94
	18.24	81.76
Mean:	16.02($\pm$1.33)	83.98($\pm$1.33)

$\frac{kt}{kp}$ = 5.28($\pm$0.48) RS_p^t = 15.73($\pm$1.45)

Summarising these results in order to obtain Arrhenius parameters:-

$T^{o}k$	$10^{-3}/T$	kt/kp	$\ln(kt/kp)$
273.5	3.66	10.61	2.36
285	3.51	9.63	2.26
297	3.37	8.68	2.16
307	3.26	8.07	2.09
317	3.16	6.35	1.85
328	3.05	5.28	1.66

Plot $\ln(kt/kp)$ vs. $1/T$ gives:

$$E_p - E_t = 2{,}220(\pm 326) \text{ cal mol}^{-1}$$

$$\ln \frac{(At)}{(Ap)} = -1.658(\pm 0.548)$$

Photochlorination of 1,1-Dichloroethane in Perdeuterobenzene and Benzene

G.L.C. Column: 12' 15% Silicone Oil on Celite at 120°C

All reactions were carried out at 20°C

Perdeuterobenzene

$\frac{(SOLVENT)}{(SUBSTRATE)} = 0.98$

% Distribution	CH_3	$CHCl_2$
	15.86	84.14
	18.45	81.55
	17.36	82.64
	13.67	86.33
Mean:	16.34(±2.07)	83.66(±2.07)

$\frac{kt}{kp} = 5.20(\pm 0.83)$ $RS_p^t = 15.60(\pm 2.48)$

$\frac{(SOLVENT)}{(SUBSTRATE)} = 2.07$

% Distribution	CH_3	$CHCl_2$
	13.73	86.27
	13.18	86.82
	15.07	84.93
	15.44	84.56
Mean:	14.36(±1.07)	85.64(±1.07)

$\frac{kt}{kp} = 6.00(\pm 0.53)$ $RS_p^t = 17.99(\pm 1.58)$

$\frac{(SOLVENT)}{(SUBSTRATE)} = 3.63$

% Distribution

CH_3	$CHCl_2$
12.64	87.36
14.04	85.96
11.86	88.14
12.27	87.73
13.84	86.16
Mean: 12.93($\pm$0.96)	87.07($\pm$0.96)

$\frac{kt}{kp} = 6.77(\pm 0.57)$ $RS_p^t = 20.30(\pm 1.72B$

$\frac{(SOLVENT)}{(SUBSTRATE)} = 6.11$

% Distribution

CH_3	$CHCl_2$
12.16	87.84
13.87	86.13
Mean: 13.02($\pm$1.21)	86.98($\pm$1.21)

$\frac{kt}{kp} = 6.71(\pm 0.72)$ $RS_p^t = 20.15(\pm 2.15)$

$\frac{(SOLVENT)}{(SUBSTRATE)} = 14.10$

% Distribution

CH_3	$CHCl_2$
9.91	90.09
9.39	90.61
12.10	87.90
10.33	89.67
10.88	89.12
10.51	89.49
Mean: 10.52($\pm$0.93)	89.45($\pm$0.93)

$\frac{kt}{kp} = 8.57(\pm 0.81)$ $RS_p^t = 25.70(\pm 2.44)$

Benzene

$\frac{(SOLVENT)}{(SUBSTRATE)} = 0.91$

CH_3 ———	$CHCl_2$
17.20	82.80
17.31	82.69
18.92	81.08
17.29	82.71
17.59	82.41
17.17	82.83
17.58($\pm$0.67)	82.42($\pm$0.67)

$\frac{kt}{kp} = 4.69(\pm 0.21)$ $RS_p^t = 14.08(\pm 0.62)$

$\frac{(SOLVENT)}{(SUBSTRATE)} = 1.88$

CH_3 ———	$CHCl_2$
11.38	88.62
13.13	86.87
13.99	86.01
12.83($\pm$1.33)	87.17($\pm$1.33)

$\frac{kt}{kp} = 6.85(\pm 0.84)$ $RS_p^t = 20.55(\pm 2.53)$

$\frac{(SOLVENT)}{(SUBSTRATE)} = 2.37$

CH_3 ———	$CHCl_2$
12.97	87.03
13.17	86.83
12.86	87.14
11.75	88.25
12.69($\pm$0.64)	87.31($\pm$0.64)

$\frac{kt}{kp} = 6.89(\pm 0.42)$ $RS_p^t = 20.69(\pm 1.25)$

$\frac{(SOLVENT)}{(SUBSTRATE)} = 4.90$

CH_3 ———	$CHCl_2$
12.03	87.97
13.44	86.56
12.79	87.21
12.75($\pm$0.71)	87.25($\pm$0.71)

$\frac{kt}{kp} = 6.85(\pm 0.43)$ $RS_p^t = 20.57(\pm 1.31)$

$\frac{(SOLVENT)}{(SUBSTRATE)} = 8.74$

CH_3 ———	$CHCl_2$
12.94	87.06
10.98	89.02
11.98	88.02
13.55	86.45
12.36($\pm$1.13)	87.64($\pm$1.13)

$\frac{kt}{} = 7.14(\pm 0.76)$ $RS_p^t = 21.42(\pm 2.28)$

For a plot of $^{kt}/kp$ vs. (Solvent)/(Substrate) see Figure 6.

Liquid Phase Photochlorination of 1,1-Dichloroethane in Various Solvents

All reactions were carried out at 20°C.

Solvent: Acetyl Chloride

(SOLVENT)/(SUBSTRATE) = 4.79

	CH_3 ———	$CHCl_2$
% Distribution	31.58	68.42
	34.96	65.05
	32.89	67.71
	31.67	68.33
	30.66	69.34
Mean:	32.23(±1.63)	67.77(±1.63)

$\frac{kt}{kp}$ = 2.11(±0.15) RS_p^t = 6.33(±0.45)

Solvent: Methylene Chloride

(SOLVENT)/(SUBSTRATE) = 5.30

	CH_3 ———	$CHCl_2$
% Distribution	28.52	71.48
	27.37	72.63
	26.68	73.32
	27.52(±0.93)	72.48(±0.93)

$\frac{kt}{kp}$ = 2.64(±0.12) RS_p^t = 7.91(±0.37)

Solvent: Neat 1,1-Dichloroethane

CH_3 ———	$CHCl_2$
25.42	74.58
24.52	75.48
24.22	75.78
27.91	72.09
25.52(±1.67)	74.48(±1.67)

$\frac{kt}{kp}$ = 2.93(±0.25) RS_p^t = 8.79(±0.74)

Solvent: Trifluoroacetic Acid

(SOLVENT)/(SUBSTRATE) = 4.42

CH_3 ———	$CHCl_2$
25.07	74.93
23.00	77.00
21.65	78.35
24.81	75.19
26.09	73.91
24.12(±1.78)	75.88(±1.78)

$\frac{kt}{kp}$ = 3.16(±0.32) RS_p^t = 9.49(±0.95)

Solvent: Acetonitrile

(SOLVENT)/(SUBSTRATE) = 6.49

CH_3 ———	$CHCl_2$
19.35	80.65
21.76	78.24
26.65	73.35
27.17	72.83
23.73(±3.80)	76.27(±3.80)

$\frac{kt}{kp}$ = 3.30(±0.71) RS_p^t = 9.90(±2.14)

Solvent: 1,1,2-Trichloro-1,2,2-Trifluoroethane

(SOLVENT)/(SUBSTRATE) = 2.83

CH_3	$CHCl_2$
20.61	79.39
21.40	78.60
20.88	79.12
19.80	80.20
20.67(±0.67)	79.33(±0.67)

$\frac{kt}{kp}$ = 3.84(±0.16) RS_p^t = 11.52(±0.47)

Solvent: Chlorobenzene

(SOLVENT)/(SUBSTRATE) = 3.34

CH_3	$CHCl_2$
16.24	83.76
14.02	85.98
14.11	85.89
15.14	84.86
14.88(±1.04)	85.12(±1.04)

$\frac{kt}{kp}$ = 5.76(±0.46) RS_p^t = 17.24(±1.38)

Solvent: Carbon Disulphide

(SOLVENT)/(SUBSTRATE) = 5.61

CH_3	$CHCl_2$
5.28	94.72
5.55	94.45
6.88	93.12
6.97	93.03
6.70	93.30
6.16	93.84
6.26(±0.72)	93.74(±0.72)

$\frac{kt}{kp}$ = 15.17(±0.72) RS_p^t = 45.50(±5.79)

Solvent: Perfluorohexane

(SOLVENT)/(SUBSTRATE)= 6.00

CH_3	$CHCl_2$
17.90	82.10
17.59	87.41
14.63	85.37
15.06	84.94
15.72	84.78
16.18(±1.48)	83.83(±1.48)

$\frac{kt}{kp}$ = 5.22(±0.56) RS_p^t = 15.67(±1.69)

Solvent: Perfluorotributylamine

(SOLVENT)/(SUBSTRATE) = 8.07

CH_3	$CHCl_2$
8.14	91.86
9.47	90.53
9.50	90.50
10.47	89.53
8.45	91.55
9.21(±0.93)	90.79(±0.93)

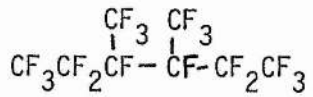
$\frac{kt}{kp}$ = 9.95(±1.10) RS_p^t = 29.85(±3.30)

Solvent: Perfluoro-N-Methyl Morpholine

(SOLVENT)/(SUBSTRATE) = 4.48

CH_3	$CHCl_2$
12.71	87.29
12.90	87.10
12.97	87.03
13.50	86.50
13.02(±0.34)	86.98(±0.34)

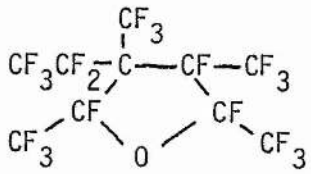
$\frac{kt}{kp}$ = 6.68(±0.20) RS_p^t = 20.05(±0.59)

Solvent: Perfluoro - 3,4-Dimethylhexane 

(SOLVENT)/(SUBSTRATE) = 8.56

	CH_3	$CHCl_2$
% Distribution	12.73	87.27
	14.17	85.83
	15.29	84.71
	14.44	85.56
Mean:	14.16(±1.06)	85.84(±1.06)

$\frac{kt}{kp}$ = 6.09(±0.55) RS_p^t = 18.28(±1.66)

Solvent: 

(SOLVENT)/(SUBSTRATE) = 7.57

	CH_3	$CHCl_2$
% Distribution	18.47	81.53
	15.85	84.15
	15.22	84.78
	19.35	80.65
Mean:	17.22(±2.00)	82.78(±2.00)

$\frac{kt}{kp}$ = 4.87(±0.68) RS_p^t = 14.60(±2.04)

Liquid Phase Photochlorination of 1,1-Dichloroethane Using t-Butyl Hypochlorite at 20°C

Solvent: 1,1,2-Trichloro-1,2,2-Trifluoroethane

(SOLVENT)/(SUBSTRATE) = 2.83

	CH_3 ———	$CHCl_2$
% Distribution	7.44	92.56
	11.23	88.77
	7.92	92.08
	9.52	90.48
Mean:	9.03(±1.71)	90.97(±1.71)

$\frac{kt}{kp}$ = 10.37(±2.06) RS_p^t = 31.11(±6.17)

Liquid Phase Photochlorination of 1,1-Dichloroethane Using Sulphuryl Chloride

$(CH_3CHCl_2)/(SO_2Cl_2)$ = 4.78

Temperature: 20°C

	CH_3 ———	$CHCl_2$
% Distribution	18.29	81.71
	18.14	81.86
	19.11	80.89
	16.12	83.88
Mean:	17.92(±1.27)	82.08(±1.27)

$\frac{kt}{kp}$ = 4.60(±0.42) RS_p^t = 13.81(±1.25)

Liquid Phase Photochlorination of 1,1,2-Trichloroethane

In all cases the reaction was carried out at 20°C and the products analysed using a 7' g.l.c. column packed with 20% Silicone Oil on Celite at a temperature of 130°C.

Solvent: Neat 1,1,2-Trichloroethane

	CH_2Cl ——	$CHCl_2$
% Distribution	49.92	50.08
	49.88	50.12
	49.85	50.15
	49.49	50.51
Mean:	49.79(±0.20)	50.21(±0.20)

$\frac{kt}{k_s} = 1.01(\pm 0.01)$

Solvent: Carbon Tetrachloride

(SOLVENT)/(SUBSTRATE) = 3.84

	CH_2Cl ——	$CHCl_2$
% Distribution	44.60	49.56
	43.80	50.53
	43.80	51.12
	44.01	50.94
Mean:	44.05(±0.38)	50.54(±0.70)

$\frac{kt}{k_s} = 1.15(\pm 0.02)$

Small amounts of penta-chloroethane are always formed in the above reaction. These may arise from the chlorination of either $CHCl_2 - CHCl_2$ or CH_2ClCCl_3.

Solvent: Benzene

(SOLVENT)/(SUBSTRATE) = 4.17

	CH_2Cl	$CHCl_2$
% Distribution	12.53	87.47
	13.01	86.99
	13.71	86.29
	12.47	87.53
	9.82	90.18
Mean:	12.31(±1.48)	87.69(±1.48)

$\frac{kt}{k_s} = 7.23(\pm 1.13)$

Discussion

The Arrhenius Parameters obtained by a least square treatment of the relative rate data are summarised in Table 1.

Table 1 - Arrhenius Parameters for Chlorination of 1,1-Dichloroethane

PHASE	(E_p-E_t)cal mol^{-1}	A_t/A_p	k_t/k_p at 30°C
GAS	1,194(±216)	1.42(±0.43)	10.30
LIQUID	910(±177)	0.59(±0.18)	2.67
BENZENE	2,220(±326)	0.19(±0.13)	7.56

The ratio of the rate constants, and in turn the selectivity, can be expressed:-

$$\frac{k_t}{k_p} = \frac{A_t}{A_p} \exp\left(\frac{(E_p-E_t)}{RT}\right)$$

Therefore, the selectivity of the reaction is determined by two factors:-

1. The difference in activation energies of the primary and tertiary hydrogen abstraction reactions, Ep-Et.
2. The ratio of the pre-exponential factors, At/Ap.

As expected, the selectivity in the gas phase at a particular temperature is greater than that in the liquid phase at the same temperature. Contrary to Marten's[32] observations, Table 1 shows that within experimental error the difference in activation energy is very similar in both the gas and neat liquid phase reactions.

The higher selectivity in the gas phase is almost entirely due to a larger ratio of pre-exponential factors compared to the liquid phase. Thus an entropy effect accounts for the lower selectivity of the liquid phase reaction. It is highly probable that in the liquid phase the transition state is solvated to some extent, decreasing the entropy of the system compared to the gas phase. These results parallel those of Tedder[17] when he determined that the change in selectivity in the gas and liquid phase chlorination of n-hexane is due to a balancing of entropic and enthalpic factors.

Table 1 also shows that benzene, a 'complexing' solvent, substantially increases the selectivity of the liquid phase reaction. Again the ratio of the rate constants is a balance of entropic and enthalpic factors. In benzene, the reaction has a much greater difference in activation energy between the two abstraction steps. This can be explained by Russell's[19] theory that the reactants are stabilized by the formation of a TT complex between the benzene and the chlorine atom. The abstraction of the primary hydrogen could well become endothermic leaving the abstraction of the tertiary hydrogen as energetically more favourable. In Marten's[29] work on the chlorination of 1,1-dichloroethane in 'complexing' solvents (in this case it was CS_2) he arrived at a value $E_p - E_t = 100(\pm 200)$ cal mol^{-1} which is in contradiction to the value in Table 1. He attributed the increased selectivity to be mainly due to entropic effects. The results here suggest quite the contrary, in fact the ratio of the pre exponential factors are much lower than the ratio in the neat liquid phase reaction. Therefore, the selectivity is not as high as would be expected from energetic considerations alone and the entropic factor partly decreases the increased selectivity. In benzene the transition state is probably even more solvated than in the neat liquid phase reaction causing a decrease in the entropy of the system.

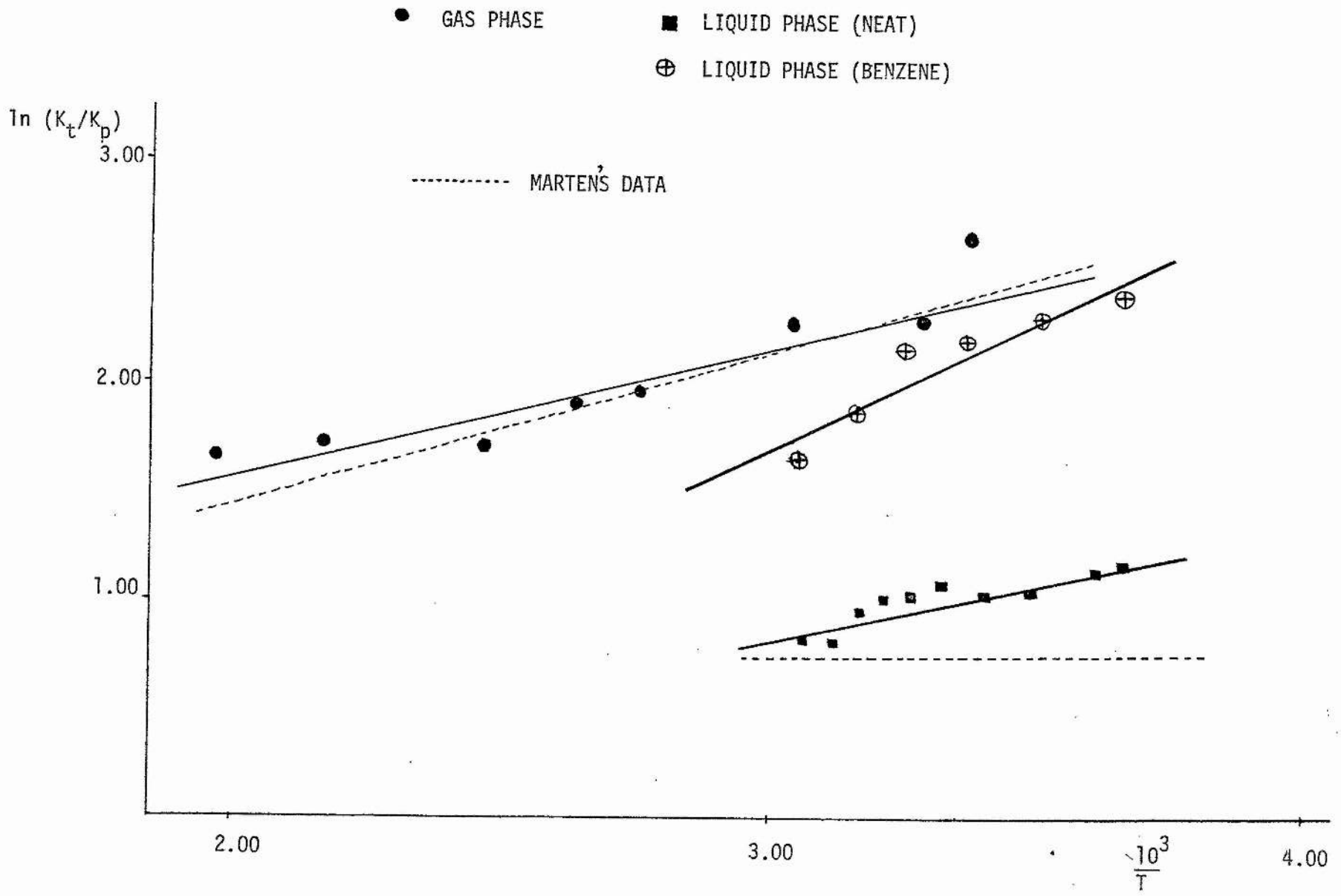
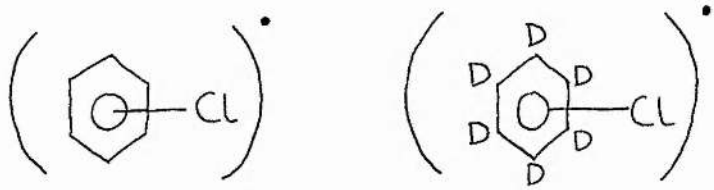

GAS PHASE
LIQUID PHASE (NEAT)
LIQUID PHASE (BENZENE)
ln (K_t/K_p)
3.00
2.00
1.00
MARTEN'S DATA
2.00
3.00
4.00
$\frac{10^3}{T}$

FIGURE 5

Figure 5 shows the temperature dependence of the photochlorination of 1,1-dichloroethane in the gas, liquid and complexing solvent phases. It also shows the plot of Marten's data for the gas and liquid phases. In fact, both sets of results do not vary that much considering the margins of error using this technique. A slight change in the slope of the graph will lead to a large change in the intercept and hence to quite different values of the pre-exponential factors.

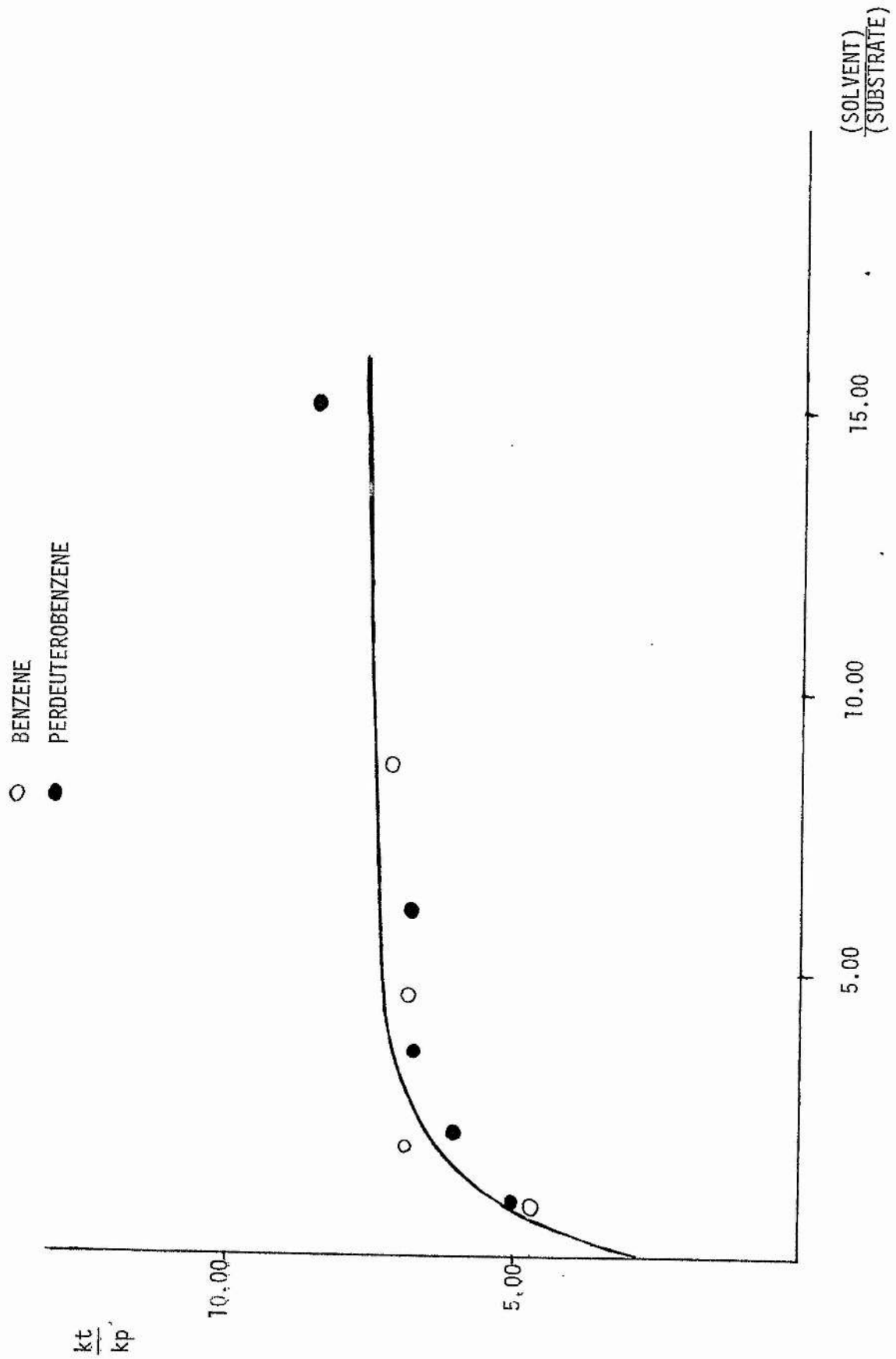
Figure 6 shows the change in selectivity obtained by chlorinating 1,1-dichloroethane over a (solvent)/(substrate) range in benzene and perdeuterobenzene. Within experimental error the results in the two solvents overlap. Following Russells[18.19] theory that the abstracting radicals are TT charge transfer complexes of the aromatic solvent and the chlorine atom they may be depicted:-



I II

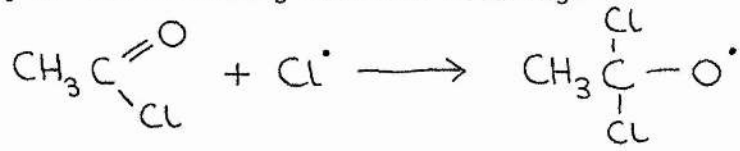
It was anticipated that the stabilization energy gained in I and II would be sufficiently different to cause a change in the selectivity of the reaction. The stability gained must be directly proportional to the strength of the charge transfer bond between the chlorine and the aromatic nucleus. There is no doubt a difference in the bond strength between structures I and II, but any difference in reaction selectivity caused by it is too small to be detected by the method used. However, figure 6 does show that the selectivity in a complexing solvent rises with increasing solvent concentration to a more or less constant value.

FIGURE 6

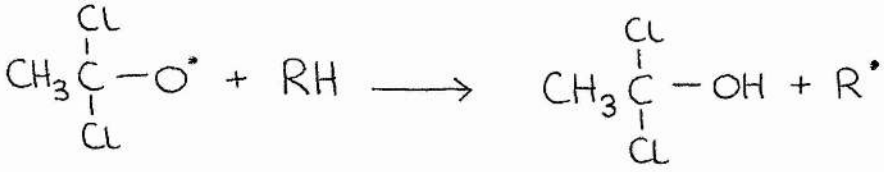

BENZENE
PERDEUTEROBENZENE
$\frac{kt}{kp}$
10.00
5.00
5.00
10.00
15.00
(SOLVENT)/(SUBSTRATE)

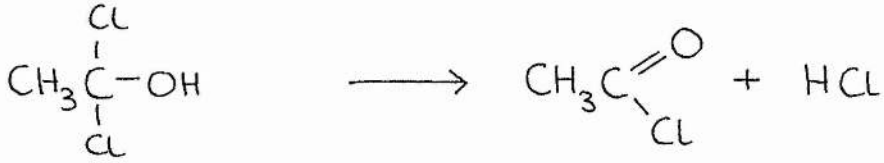
This is the result that would be expected if there is an equilibrium between the solvent and the reactants. Once the concentration of solvent has reached a certain level the equilibrium will be totally on the side of the solvated radical and no increase in the selectivity of the reaction can be expected.

Table 2 shows the selectivity of the reaction at room temperature in a wide variety of solvent systems. There was found to be no real correlation between the selectivity and solvent viscosity or polarity. Within the range of experimental error the selectivity does not change too much in the aliphatic solvents used. However, acetyl chloride does seem to cause a slight, but noticable, decrease in selectivity. An explanation could be that there is a solvation effect in the transition state which affects the entropy and hence alters the ratios of the pre-exponential factor giving decreased selectivity. This can perhaps be further elaborated by considering the possibility of the following reaction occuring:-



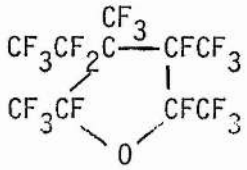
III





The radical III, is the species doing the hydrogen abstracting.

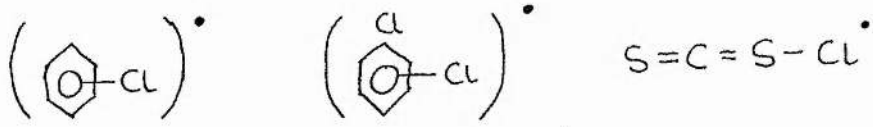
Table 2 - Selectivity for Chlorination of 1,1-Dichloroethane In Various Solvents at 20°C

Solvent	(SOLVENT) / (1,1-DICHLOROETHANE)	RS_p^t
Acetyl Chloride	4.79	6.33
Methylene Chloride	5.30	7.91
None	--	8.79
Tri fluoroacetic Acid	4.42	9.49
Acetonitrile	6.49	9.90
1,1,2-Trichloro-1,2,2-Trifluoroethane	2.83	11.52
Chlorobenzene	3.34	17.24
* Benzene	5.00	21.75
Carbon Disulphide	5.61	45.50
Perfluorohexane	6.00	15.67
Perfluorotributylamine	8.07	29.85
Perfluoro N methyl morpholine	4.48	20.05
Perfluoro-3,4 Dimethyl hexane	8.56	18.28
	7.57	14.60

* From extrapolation

In abstracting the hydrogen atom on carbon 1 in 1,1-dichloroethane there is a possibility of steric hindrance which would become apparent through a decrease in the PZ factor. Attack on the hydrogens at carbon 2 would be faster and an overall decrease in selectivity would occur. Similar effects have been reported for t-butoxy radicals in acetic acid.[53]

The 'complexing' solvents used: benzene, chlorobenzene and carbon disulphide all give increased selectivity with carbon disulphide being the most selective solvent. The abstracting species must be:-



I IV V

Results already discussed indicate that in these complexing systems the increased selectivity is a mainly energetic effect. The energy gained from forming the complexed radicals causes a much greater difference in activation energy between the primary and tertiary hydrogen abstraction steps. In all cases there is probably a lowering of entropy, due to solvation, which tends to decrease selectivity partly counter-balancing the overall increase in selectivity.

The use of perfluorinated solvents yields very interesting results. Without exception they all give greater selectivity than the neat liquid phase reaction, some more so than others. The thinking behind using perfluorinated solvents was to introduce an inert solvent which would break up any solvation in the reactants and give 'gas phase' conditions in the liquid phase. To some extent this reasoning has been justified and some of the selectivities shown in table 2 are approaching those that would be anticipated in the gas phase at room temperature.

Table 3 shows the change in selectivity obtained in the liquid phase when other radicals are used for the abstraction of hydrogen.

Table 3 - Selectivity of Chlorination of 1,1-Dichloroethane In Liquid Phase Using $Cl^{\bullet}$, $SO_2Cl^{\bullet}$, $(CH_3)_3CO^{\bullet}$

RADICAL	SOURCE	RS_p^t
$Cl^{\bullet}$	Cl_2	8.79
$SO_2Cl^{\bullet}$	SO_2Cl_2	13.81
$Bu^tO^{\bullet}$	Bu^tOCl	31.11

Sulphuryl chloride is a useful chlorinating agent and the free radical process is initiated using ultra violet light. The chain propagation reactions are:-

$$SO_2Cl^{\bullet} + RH \longrightarrow R^{\bullet} + HCl + SO_2$$

$$R^{\bullet} + SO_2Cl_2 \longrightarrow RCl + SO_2Cl^{\bullet}$$

Table 3 shows that when it is used to chlorinate 1,1-dichloroethane it does slightly increase the selectivity. There is not a dramatic increase in selectivity because it has been shown that there is an equilibrium.[33]

$$SO_2Cl^{\bullet} \rightleftharpoons SO_2 + Cl^{\bullet}$$

Consequently much of the reaction can take place with the chlorine atom rather than the chlorosulphonyl radical. The selectivity will be determined by the position of the equilibrium. The reason for the increased selectivity can again be thought of in terms of Russell's[18,19] complex theory. Here the chlorine atom is solvated by sulphur dioxide and the reactants will be stabilised energetically making the tertiary abstraction step more favourable.

This explanation is favoured because Russell[34] observed that the selectivities of chlorination in benzene by molecular chlorine and sulphuryl chloride are identical. Here the chlorine atom can be solvated by benzene or sulphur dioxide but at increasing benzene concentration the reaction will proceed almost entirely in the benzene solvated radical.

t-Butyl hypochlorite is another useful chlorinating agent. It is easily split by photolysis into a t-butoxy radical and a chlorine atom. The chain propogation reactions are:-

$$Bu^tO^\bullet + RH \rightarrow R^\bullet + Bu^tOH$$
$$R^\bullet + Bu^tOCl \rightarrow RCl + Bu^tO^\bullet$$

Table 3 shows that when t-butoxy radicals abstract the hydrogen atoms during the chlorination of 1,1-dichloroethane a much higher selectivity ensues. The abstraction of hydrogen by $Cl^\bullet$ and $tBuO^\bullet$ from a substituted alkane are both equally exothermic. The activation energies are higher when $Bu^tO^\bullet$ radicals are used i.e. the value of α in the Evans-Polanyi[12] relation is much higher than the 0.1 determined for chlorine atoms. Therefore there is more bond breaking in the transition state and the strength of the C-H bonds are much more important. The greater selectivity in the chlorination of 1,1-dichloroethane by t-butyl hypochlorite must be a reflection of differing bond strength more than the de-activation of the 2 position due to the repulsive polar effect and the activation of the 1 position because of resonance stabilization.

The results for the liquid phase chlorination of 1,1,2-trichloroethane are shown in Table 4.

Table 4 - Liquid Phase Photochlorination of 1,1,2-Trichloroethane

SOLVENT	$k1/k2$	RS_2^1
NONE	1.01	2.02
CARBON TETRACHLORIDE	1.15	2.30
BENZENE	7.23	14.46

Firstly considering the situation in non complexing media there seems to be almost equal attack at positions 1 & 2. This can be compared to the attack in 1,1-dichloroethane.

	$CHCl_2CH_3$		$CHCl_2CH_2Cl$	
$k1/k2$	2.7	1.0	1.1	1.0

It can be seen that the introduction of a chlorine substituent at position 2 causes a lowering of the reaction selectivity. This is because resonance stabilization of the radical can now take place at position 2 as well as position 1, thus increasing the reactivity of position 2. In terms of repulsive polar effect, in 1,1-dichloroethane - $CHCl_2$ deactivates position 2 much more than - CH_3 deactivates position 1 so a reasonable difference in reactivity can be expected. In 1,1,2-trichloroethane - $CHCl_2$ deactivates position 2 only slightly more than - CH_2Cl deactivates position 1. When these two opposing effects take effect position 2 in 1,1,2-trichloroethane becomes relatively more reactive and so $k1/k2 \sim 1$.

In 'complexing' solvent however, there is a great deal of attack at position 1 in 1,1,2-trichloroethane. Comparing the reactivities with those of 1,1-dichloroethane in benzene we have:-

	$CHCl_2$	CH_3	$CHCl_2$	CH_2Cl
$k1/k2$	7.25	1.00	7.23	1.00

In effect the reactivities of the 1 positions compared to the 2 positions are very much the same. In 1,1,2-trichloroethane the introduction of a chlorine substituent at position 2 would be expected to deactivate position 1 and lower its relative reactivity. The probably explanation of these results lies in the energetics of the reactions. In non-complexing media the increased reactivity of position 2 must be due to a small activation energy difference giving lower selectivity. When the two chlorination reactions are done in benzene there must be such a relatively large energetic stabilization of the reactants that the differences in activation energies are very much increased in both cases. The difference is so large compared to the small change .....

..... going from $CHCl_2CH_3$ to $CHCl_2CH_2Cl$ that both reactions have similar selectivity. This can best be shown diagramatically:-

FIGURE 7 Chlorination of 1,1-Dichloroethane

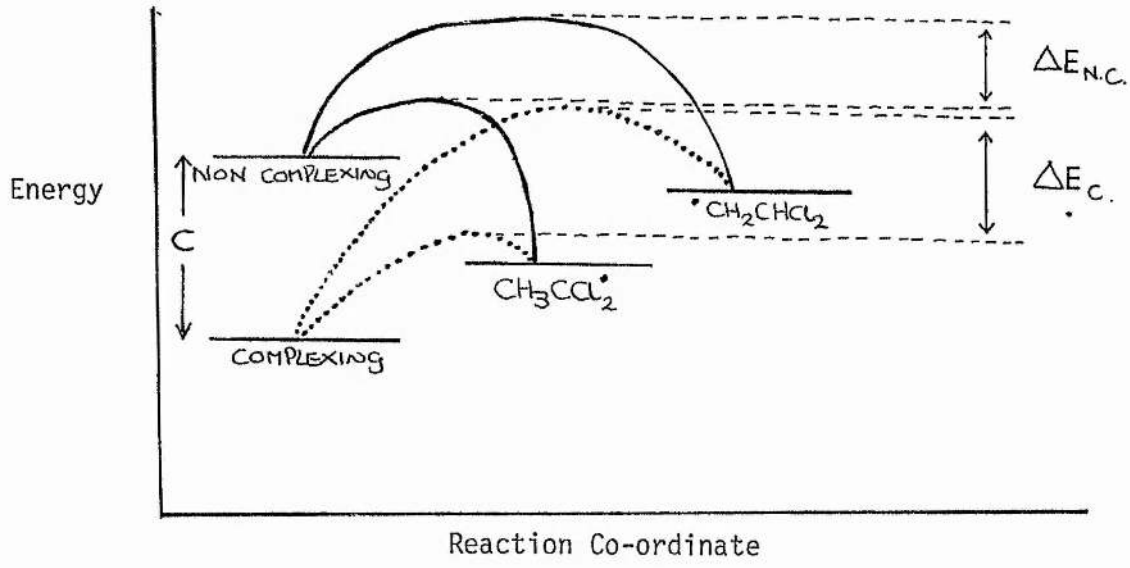
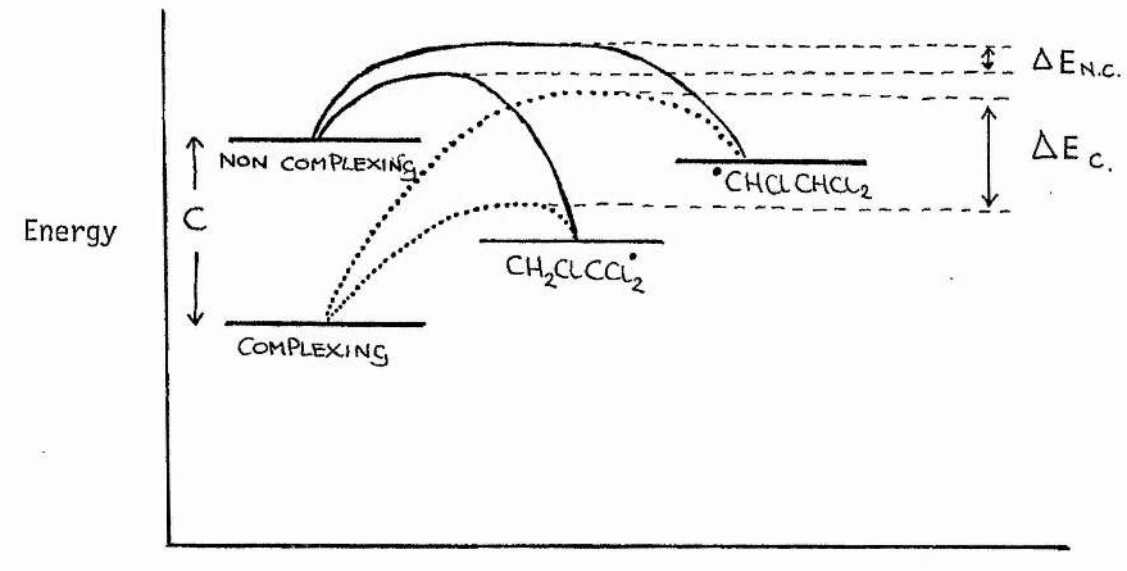


FIGURE 8 Chlorination of 1,1,2-Trichloroethane



The diagrams show that for non-complexing media:-

$$(\Delta E_{N.C})_{1,1\text{-Dichloroethane}} > (\Delta E_{N.C})_{1,1,2\text{-Trichloroethane}}$$

Therefore there is more selectivity in the chlorination of 1,1-dichloroethane.

However, in complexing media:-

$$(\Delta E_{C})_{1,1\text{-Dichloroethane}} \sim (\Delta E_{C})_{1,1,2\text{-Trichloroethane}}$$

and consequently the selectivities of the two reactions are very similar.

PART TWO

The Chlorination of 1-Substituted Butanes

PART TWO

'The Chlorination of 1-Substituted Butanes'

INTRODUCTION

The directive effects in the atomic chlorination of substituted butanes has received considerable study. Early work was complicated by the occurence of both atomic and ionic substitution. Ionic substitition occurs via the Hell-Volhard-Zelinsky[35] reaction for the chlorination of carboxylic acid derivatives and yields the α-chloro derivative. Much of the work in this field has been carried out in the gas phase so as to achieve radical attack. Substituted alkanes such as halides, acid chlorides and nitriles can be chlorinated in both gas and liquid phases without the incursion of polar reactions provided catalysts such as phosphorus halides or iodine are avoided. Earlier work was also hampered by the necessity of separating the reaction products by fractional distillation to establish the distribution of the chlorinated products. Since the advent of gas liquid chromatography, the analysis of product distribution has been both easier and more accurate.

In this section the directive effects in the atomic chlorination of 1-chlorobutane, 1-fluorobutane, 1,1,1-trifluoropentane, 1-valeronitrile and the acid chlorides of valeric, hexanoic and heptanoic acids receive further study. The chlorination of 1-chlorobutane was quite extensively investigated in both gas and solvent phases. The main reason for this was to provide a comparison with the study on 1,1-dichloroethane done in Part One. Another was to re-investigate some of the earlier gas phase work done in this laboratory by Fredericks[36], using a flow system. It was thought important to see how his results compare with those obtained fromthe present static system.

The first useful work on the gas phase chlorination of 1-chlorobutane was done by Fredericks and Tedder[36] who used gas liquid chromatography to analyse the product mixture. The liquid phase chlorination, using sulphuryl chloride as the chlorinating agent, was studied by Brown and Ash.[37,38] This was later re-examined, using g.l.c. analysis by Horner and Schlafer.[39] The effect of complexing and non-complexing media on the atomic chlorination of 1-chlorobutane was discussed by Walling and Mayahi[16] Later, Walling[40] investigated the liquid phase chlorination of 1-chlorobutane using t-butyl hypochlorite. The gas phase chlorination using this reagent was studied much later by Stoddart and Nechvatal.[41] The selective liquid phase chlorination using iodobenzene dichloride has been discussed by Tanner et al.[42]

It has been shown that substituents may accelerate or retard free radical substitution at various points along an alkane chain. In the case of gas phase atomic chlorination the carbon atoms α and β to the substituent at the 1 position are almost exclusively deactivated to attack. The deactivation, caused by the inductive effect of the substituent, may be compensated at the α position because of resonance stabilisation. Table 5 shows the relative reactivities for the gas phase chlorination of the 1-substituted butanes under study in this section.

Table 5 Relative Selectivities RS_p^s for chlorination of 1-substituted butanes at 50°c in gas phase

CH_3	— CH_2	— CH_2	— CH_2	— X	Reference
1.0	3.6	3.6	1.0	- H	36
1.0	3.7	2.1	0.8	- Cl	36
1.0	3.7	1.7	0.9	- F	36
1.0	4.3	1.2	0.04	- CF_3	43
1.0	3.9	1.7	0.2	- CN	44
1.0	3.9	2.1	0.2	- COCl	45

Within reason, the deactivation can be seen to extend only as far as the β position. This was confirmed by Singh and Tedder[46,23] when they investigated the gas phase chlorination of the acid fluorides of valeric, hexanoic and heptanoic acids. When the reaction was carried out in the liquid phase the deactivation effect was seen right along the chain.

The object of the work described in this section is to extend the gas phase results to the liquid phase in both complexing and non-complexing solvents. There seems to have been no investigation into the liquid phase chlorination of 1-fluorobutane and 1,1,1-trifluoropentane. Rouchaud and Bruylants[47] have partly studied the liquid phase chlorination of valeronitrile but do not seem to have extended their study to complexing media. The liquid phase chlorination of the acid chlorides has been studied to some extent by Singh and Tedder[23,45,46] and Den Hertog[48,49] et al.

It was thought necessary to reappraise this work in order to be able to make a direct comparison with the results from the other 1-substituted butanes.

EXPERIMENTAL

MATERIALS

As in Part One chlorine was used as supplied from British Oxygen Company. The 1-chlorobutane (Hopkins and Williams) was purified by distillation on a Bucchi spinning band column and the purity checked by gas liquid chromatography. Again all the solvents were used as supplied by the manufacturer. Trichloromethyl sulphonyl chloride (Fluka) was used as supplied and t-butyl hypochlorite synthesised as in Part One. Valeryl chloride, hexanoyl chloride, heptanoyl chloride and valeronitrile were all used as supplied by the Aldrich Chemical Company. 1-fluorobutane and 1,1,1-trifluoropentane were synthesised as follows:-

Preparation of 1-fluorobutane[50]

Redistilled Dimethyl formamide (80ml) was placed in a 250ml round bottomed flask along with anhydrous potassium fluoride (23g). A stirrer, dropping funnel and 4 step Vigreux column were attached to the 3 necked flask. The Vigreux column was fitted with a still head, thermometer and a condenser leading to a round bottomed flask (50ml) immersed in an ice/salt mixture. The contents of the 250ml round bottomed flask were heated to 130°C then 1-bromobutane (20ml) added. The 1-fluorobutane was collected in the 50ml round bottomed flask. It was purified by preparative gas liquid chromatography using a 12' glass column packed with 25% T.T.P. on 'Embacel' at 90°C.

1-fluorobutane

n.m.r. δ = 0.9 (triplet, J = 12Hz, 3H, $\underline{CH_3}CH_2CH_2CH_2F$)

δ = 1.2 - 1.9 (complex, 4H, $CH_3\underline{CH_2CH_2}CH_2F$)

δ = 4.1 and 4.7 (doublet of triplets, J_{H-F} = 46 Hz, J_{H-H} = 12 Hz, 2H, $CH_3CH_2CH_2\underline{CH_2}F$)

Preparation of 1,1,1-trifluoropentane[51]

Crude 1,1,1-trifluoropentane was supplied by I.C.I. Mond Division. It was prepared by reacting valeric acid with sulphur tetrafluoride at elevated temperature under pressure in a stainless steel autoclave. The reaction is a two step process:

$$RCOOH + SF_4 \longrightarrow RCOF + HF + SOF_2$$

$$RCOF + SF_4 \longrightarrow RCF_3 + SOF_2$$

The crude product was distilled at reduced pressure on a vaccuum line and an almost pure product was produced.

1,1,1-trifluoropentane

n.m.r. δ = 0.9 (triplet, J = 14 Hz, 3H, $\underline{CH_3}CH_2CH_2CH_2CF_3$)

δ = 1.1 - 1.6 (complex, 4H, $CH_3\underline{CH_2}\underline{CH_2}CH_2CF_3$)

δ = 1.9 - 2.1 (complex, 2H, $CH_3CH_2CH_2\underline{CH_2}CF_3$)

APPARATUS AND PROCEDURE

Gas Phase Reactions: Gas phase experiments were carried out on the same static system described in Part One. The experimental procedure was also the same.

Liquid Phase Reactions: All reactions in the liquid phase were carried out in the same way as described in Part One with the exception of the chlorination of 1-chlorobutane by trichloromethyl sulphonyl chloride. In this case, the reaction mixture was distilled under reflux overnight and the radical chain reaction initiated by benzoyl peroxide.

ANALYSIS OF THE PRODUCTS

The products of all the reactions were analysed by gas liquid chromatography. The same system was used that has been described in Part One. Two types of column were used: a 12' glass column packed with 15% silicone oil stationary phase on 100/120 mesh 'Celite' and a 12' glass column packed with 25% tritolyl phosphate (T.T.P.) stationary phase on 80/100 mesh 'Embacel'.

The products of the photochlorination of valeryl, hexanoyl and heptanoyl chlorides were more easily separated by converting them to the corresponding methyl esters by the addition of methanol. In some cases two layers would form on the addition of methanol. One of these layers was the solvent and this was removed from the ester layer by a Buchii rotary evaporator.

The products of the chlorination of 1-chlorobutane were identified by comparing their retention times with those of authentic compounds. The elution order for the products of the chlorination of valeryl, hexanoyl, heptanoyl chlorides and valeronitrile had already been determined in this laboratory[60] and so the products were identified immediately. In all cases the elution order was established to be 1,1-. 1,2-, 1,3- and 1,4- dichloro products. Therefore it was assumed that the dichlorination products of 1-fluorobutane and 1,1,1-trifluoropentane would elute in the same order.

Gas phase photochlorination of 1-chlorobutane

G.L.C. column: 12' 15% silicone oil on "Celite'.
Oven temperature: 125°C

Reaction temperature: 60°C

	CH_3 —	CH_2 —	CH_2 —	CH_2Cl
% Distribution	17.39	48.11	26.34	8.16
	17.96	49.03	25.24	7.79
Mean:	17.68(±0.40)	48.57(±0.65)	25.79(±0.77)	7.96(±0.28)
$\frac{Kx}{K_4}$	1.00	2.75	1.46	0.45
RS_p^s	1.00	4.12(±0.04)	2.19(±0.11)	0.68(±0.04)

Reaction Temperature: 90°C

	CH_3 —	CH_2 —	CH_2 —	CH_2Cl
% Distribution	18.94	51.58	22.11	7.37
	19.84	51.59	21.43	7.14
	18.54	54.15	20.98	6.34
	20.00	50.62	23.13	6.25
Mean:	19.33(±0.70)	51.99(±1.51)	21.91(±0.94)	6.78(±0.56)
$\frac{Kx}{K_4}$	1.00	2.69	1.13	0.35
RS_p^s	1.00	4.04(±0.26)	1.70(±0.06)	0.53(±0.05)

Reaction Temperature: 135°C

	CH_3 —	CH_2 —	CH_2 —	CH_2Cl
% Distribution	17.07	53.05	21.95	7.93
	18.03	51.91	22.95	7.10
	18.32	52.36	23.04	6.28
Mean:	17.81(±0.65)	52.44(±0.57)	22.65(±0.61)	7.10(±0.83)
$\frac{Kx}{K_4}$	1.00	2.95	1.27	0.40
RS_p^s	1.00	4.42(±0.21)	1.90(±0.04)	0.60(±0.10)

Reaction Temperature: 170°C

	CH_3 —	CH_2 —	CH_2 —	CH_2Cl
% Distribution	18.09	50.53	22.34	9.04
	19.85	48.09	22.14	9.92
	18.48	49.46	22.83	9.24
	18.75	48.56	22.60	10.10
Mean:	18.79(±0.76)	49.16(±1.08)	22.48(±0.30)	9.58(±0.51)
$\frac{Kx}{K_4}$	1.00	2.62	1.20	0.51

RS_p^s	1.00	3.93(±0.24)	1.80(±0.09)	0.77(±0.03)

Summarising these results:

Table 6 RS_p^s values for the gas phase chlorination of 1-chlorobutane

Temperature °C	Relative Selectivity			
	CH_3 ———	CH_2 ———	CH_2 ——	CH_2Cl
60	1.00	4.12	2.19	0.68
90	1.00	4.04	1.70	0.53
135	1.00	4.42	1.90	0.60
170	1.00	3.93	1.80	0.77

These results are too scattered to give a meaningful Arrhenius plot of $\ln(kx/k_4)$ against $1/T$.

Liquid phase photochlorination of 1-chlorobutane

G.L.C. column: 12' 15% silicone oil on 'Celite'
Oven temperature: 125°C

Reaction temperature: 0.5°C

	CH_3 —	CH_2 —	CH_2 —	CH_2Cl
% Distribution:	23.22	48.93	22.14	5.72
	23.68	49.63	20.95	5.74
	24.39	47.67	22.40	5.54
	23.68	48.95	21.82	5.55
	24.11	48.34	21.76	5.79
Mean:	23.82(±0.45)	48.70(±0.75)	21.81(±0.55)	5.67(±0.12)
$\frac{Kx}{K_4}$	1.00	2.06	0.91	0.24
RS_p^s	1.00	3.09(±0.10)	1.37(±0.04)	0.36(±0.01)

Reaction temperature: 20°C

	CH_3 —	CH_2 —	CH_2 —	CH_2Cl
% Distribution:	25.32	46.11	22.76	5.80
	24.94	44.90	24.43	5.73
	26.34	44.46	22.89	6.31
	24.65	45.60	23.06	6.69
Mean:	25.31(±0.74)	45.27(±0.73)	23.29(±0.77)	6.13(±0.45)
$\frac{Kx}{K_4}$	1.00	1.79	0.92	0.25
RS_p^s	1.00	2.68(±0.11)	1.38(±0.07)	0.37(±0.03)

Reaction temperature: 33°C

	CH_3 —	CH_2 —	CH_2 —	CH_2Cl
% Distribution:	25.31	44.19	24.07	6.44
	24.38	45.51	23.35	6.76
	25.53	45.69	22.26	6.51
	25.62	45.58	22.33	6.47
	25.23	45.38	22.65	6.74
Mean:	25.21(±0.49)	45.27(±0.61)	22.93(±0.77)	6.58(±0.15)
$\frac{Kx}{K_4}$	1.00	1.79	0.91	0.26
RS_p^s	1.00	2.69(±0.07)	1.37(±0.06)	0.39(±0.02)

Reaction temperature: 44°C

	CH_3 —	CH_2 —	CH_2 —	CH_2Cl
% Distribution:	26.25	43.52	22.61	7.62
	24.32	45.22	22.99	7.47
	25.64	44.94	22.64	6.78
	26.44	44.81	21.95	6.80
	26.01	43.90	23.50	6.58
Mean:	25.73(±0.84)	44.48(±0.73)	22.74(±0.57)	7.05(±0.46)
$\frac{Kx}{K_4}$	1.00	1.73	0.89	0.27
RS_p^s	1.00	2.60(±0.12)	1.33(±0.07)	0.41(±0.03)

Reaction temperature: 52°C

	CH_3 —	CH_2 —	CH_2 —	CH_2Cl
% Distribution:	25.68	42.95	23.52	7.86
	24.99	43.81	22.82	8.37
	24.95	43.49	24.31	7.25

	25.63	43.97	23.04	7.36
Mean:	25.31(±0.40)	43.56(±0.45)	23.42(±0.60)	7.71(±0.51)
$\frac{Kx}{K_4}$	1.00	1.72	0.93	0.31
RS_p^s	1.00	2.58(±0.05)	1.39(±0.05)	0.47(±0.04)

Table 7 RS_p^s values for liquid phase chlorination of 1-chlorobutane

Temperature °C	Relative Selectivities			
	CH_3 —— CH_2 ——		CH_2 —— CH_2Cl	
0.5	1.00	3.09	1.37	0.36
20	1.00	2.68	1.38	0.37
33	1.00	2.69	1.37	0.39
43	1.00	2.60	1.33	0.41
52	1.00	2.58	1.39	0.47

Tabulating the results in order to calculate Arrhenius parameters:

$\frac{10^3}{T}$	$\ln\left(\frac{K_3}{K_4}\right)$	$\ln\left(\frac{K_2}{K_4}\right)$	$\ln\left(\frac{K_1}{K_4}\right)$
3.66	0.72	-0.09	-1.43
3.41	0.58	-0.08	-1.39
3.27	0.58	-0.09	-1.35
3.16	0.55	-0.12	-1.31
3.08	0.54	-0.07	-1.17

Plotting $\ln(Kx/k_4)$ vs $^{1}/_{T}$ gives:

$E_4 - E_3 = 593(\pm 127)$ cal mol^{-1}, $\ln\left(\frac{A_3}{A_4}\right) = -0.393(\pm 0.213)$

$E_4 - E_2 = 8(\pm 93)$ cal mol^{-1}, $\ln\left(\frac{A_2}{A_4}\right) = -0.104(\pm 0.157)$

$E_4 - E_1 = -760(\pm 245)$ cal mol^{-1}, $\ln\left(\frac{A_1}{A_4}\right) = -0.063(\pm 0.407)$

Liquid phase chlorination of 1-chlorobutane in benzene

G.L.C. column: 12' 15% silicone oil on 'Celite'
Oven temperature: 125°C

$\frac{(SOLVENT)}{(SUBSTRATE)} = 4.71$

Reaction temperature: 0.5°C

	CH_3 —	CH_2 —	CH_2 —	CH_2Cl
% Distribution:	16.14	59.06	19.74	5.06
	16.75	59.63	19.37	4.23
	17.59	58.59	19.45	4.37
	16.44	58.37	20.44	4.75
Mean:	16.73(±0.63)	58.91(±0.56)	19.75(±0.49)	4.60(±0.38)
$\frac{kx}{K_4}$	1.00	3.53	1.18	0.28
RS_p^s	1.00	5.29(±0.21)	1.77(±0.09)	0.42(±0.04)

Reaction temperature: 36°C

	CH_3 —	CH_2 —	CH_2 —	CH_2Cl
	16.89	56.99	20.62	5.55
	16.18	58.47	20.15	5.20
	17.11	58.11	19.68	5.10
	16.11	57.54	20.93	5.42
	16.80	57.78	20.64	4.78
Mean:	16.62(±0.45)	57.78(±0.56)	20.40(±0.49)	5.21(±0.30)
$\frac{Kx}{K_4}$	1.00	3.47	1.23	0.31
RS_p^s	1.00	5.21(±0.17)	1.84(±0.08)	0.47(±0.03)

Reaction temperature: 42.5°C

	CH_3 —	CH_2 —	CH_2 —	CH_2Cl
% Distribution:	16.85	56.95	21.01	5.19
	16.95	56.56	20.79	5.69
	17.99	56.52	19.58	5.91
	18.69	56.03	20.21	5.07
	16.43	58.13	19.68	5.75
Mean:	17.38(±0.93)	56.84(±0.79)	20.25(±0.64)	5.52(±0.37)
$\frac{Kx}{K_4}$	1.00	3.23	1.17	0.32
RS_p^s	1.00	4.92(±0.32)	1.75(±0.12)	0.48(±0.04)

Reaction temperature: 51.5°C

	CH_3 —	CH_2 —	CH_2 —	CH_2Cl
% Distribution:	19.47	54.08	20.52	5.93
	17.42	54.72	22.10	5.76
	18.45	53.83	21.66	6.06
	19.19	53.79	20.82	6.21
	19.00	52.83	21.72	6.44
Mean:	18.71(±0.81)	53.85(±0.68)	21.36(±0.66)	6.08(±0.26)
$\frac{Kx}{K_4}$	1.00	2.89	1.15	0.33
RS_p^s	1.00	4.33(±0.23)	1.72(±0.12)	0.49(±0.02)

Table 8 RS_p^s values for the chlorination of 1-chlorobutane in benzene

Temperature °C	Relative Selectivities CH_3 —	CH_2 —	CH_2 —	CH_2Cl
0.5	1.00	5.29	1.77	0.42
36	1.00	5.21	1.84	0.47
42.5	1.00	4.92	1.75	0.48
51.5	1.00	4.33	1.72	0.49

Tabulating these results in order to obtain Arrhenius parameters

$\frac{10^3}{T}$	$\ln(\frac{k_3}{k_4})$	$\ln(\frac{k_2}{k_4})$	$\ln(\frac{k_1}{k_4})$
3.66	1.26	0.17	-1.27
3.24	1.25	0.20	-1.16
3.17	1.19	0.15	-1.14
3.08	1.06	0.14	-1.12

Plotting $\ln(kx/k_4)$ vs $^{1}/_{T}$ gives:

$E_4 - E_3 = 505(\pm 356)$ cal mol^{-1}, $\ln(\frac{A_3}{A_4}) = 0.356(\pm 0.589)$

$E_4 - E_2 = 72(\pm 135)$ cal mol^{-1}, $\ln(\frac{A_2}{A_4}) = 0.046(\pm 0.225)$

$E_4 - E_1 = -519(\pm 8)$ cal mol^{-1}, $\ln(\frac{A_1}{A_4}) = -0.315(\pm 0.013)$

Liquid phase photochlorination of 1-chlorobutane in various solvents

All reactions were carried out at 20°C

Solvent: Acetyl chloride
(SOLVENT)/(SUBSTRATE) = 5.91

	CH_3 —	CH_2 —	CH_2 —	CH_2Cl
% Distribution:	27.18	48.59	20.04	4.19
	25.45	46.05	22.67	5.83
	24.80	47.44	22.88	4.88
Mean:	25.81(±1.23)	47.36(±1.27)	21.86(±1.58)	4.97(±0.82)
$\frac{Kx}{K_4}$	1.00	1.84(±0.07)	0.85(±0.10)	0.19(±0.04)
RS_p^s	1.00	2.76(±0.10)	1.28(±0.15)	0.29(±0.06)

Solvent: Carbon tetrachloride
(SOLVENT/(SUBSTRATE) - 3.96

	CH_3 —	CH_2 —	CH_2 —	CH_2Cl
% Distribution:	29.09	42.70	22.83	5.38
	28.03	43.21	22.82	5.94
	29.01	42.02	23.15	5.82
Mean:	28.71(±0.59)	42.64(±0.60)	22.93(±0.19)	5.71(±0.29)
$\frac{Kx}{K_4}$	1.00	1.49(±0.05)	0.80(±0.01)	0.20(±0.01)
RS_p^s	1.00	2.23(±0.07)	1.20(±0.02)	0.30(±0.02)

Neat 1-chlorobutane

	CH_3 —	CH_2 —	CH_2 —	CH_2Cl
% Distribution:	25.32	46.11	22.76	5.80
	24.94	44.90	24.43	5.73
	26.34	44.46	22.89	6.31
	24.65	45.60	23.06	6.69
Mean:	25.31(±0.74)	45.27(±0.73)	23.39(±0.77)	6.13(±0.45)
$\frac{Kx}{K_4}$	1.00	1.79(±0.07)	0.92(±0.05)	0.24(±0.02)
RS_p^s	1.00	2.68(±0.11)	1.38(±0._7)	0.36(±0.03)

Solvent: 1,1,2-trichloro-1,2,2-trifluoroethane
(SOLVENT)/(SUBSTRATE) = 3.44

	CH_3 —	CH_2 —	CH_2 —	CH_2Cl
% Distribution:	25.31	45.06	23.76	5.87
	24.58	46.21	22.52	6.69
	23.90	46.68	23.80	5.62
Mean:	24.60(±0.71)	45.98(±0.83)	23.36(±0.73)	6.06(±0.50)
$\frac{Kx}{K_4}$	1.00	1.87(±0.09)	0.95(±0.04)	0.25(±0.02
RS_p^s	1.00	2.81(±0.13)	1.42(±0.06)	0.37(±0.03)

Solvent: Nitrobenzene
(SOLVENT)/(SUBSTRATE) = 4.08

	CH_3 —	CH_2 —	CH_2 —	CH_2Cl
% Distribution:	21.94	49.93	24.09	4.04
	20.89	49.95	26.03	3.13
	22.74	51.87	21.67	3.72

Mean:	21.86(±0.93)	50.58(±1.11)	23.93(±2.18)	3.63(±0.46)
$\frac{Kx}{K_4}$	1.00	2.31(±0.70)	1.10(±0.15)	0.17(±0.02)
RS_p^s	1.00	3.47(±0.10)	1.65(±0.22)	0.25(±0.03)

Solvent: Benzene
(SOLVENT)/(SUBSTRATE) = 4.70

	CH_3 —	CH_2 —	CH_2 —	CH_2Cl
% Distribution:	15.73	59.44	20.76	4.07
	15.36	59.48	21.22	3.95
	13.96	60.36	22.17	3.52
Mean:	15.02(±0.93)	59.76(±0.52)	21.38(±0.72)	3.85(±0.29)
$\frac{Kx}{K_4}$	1.00	3.99(±0.29)	1.43(±0.14)	0.26(±0.01)
RS_p^s	1.00	5.99(±0.44)	2.14(±0.21)	0.39(±0.01)

Solvent: Carbon disulphide
(SOLVENT)/(SUBSTRATE) = 6.93

	CH_3 —	CH_2 —	CH_2 —	CH_2Cl
% Distribution:	9.67	64.23	21.06	5.04
	11.47	63.73	19.57	5.31
	10.33	64.00	19.85	5.81
Mean:	10.48(±0.88)	63.99(±0.25)	20.16(±0.79)	5.38(±0.39)
$\frac{Kx}{K_4}$	1.00	6.13(±0.55)	1.93(±0.24)	0.51(±0.05)
RS_p^s	1.00	9.19(±0.82)	2.90(±0.36)	0.77(±0.08)

Solvent: Perfluoro-N-Methyl morpholine

(SOLVENT)/(SUBSTRATE) = 5.65

	CH_3 —	CH_2 —	CH_2 —	CH_2Cl
% Distribution:	20.20	45.86	25.43	8.42
	21.97	45.43	25.01	7.60
	21.67	44.04	24.99	9.30
Mean:	21.28(±0.95)	45.11(±0.95)	25.14(±0.25)	8.44(±0.85)
$\frac{Kx}{K_4}$	1.00	2.12(±0.13)	1.18(±0.07)	0.40(±0.04)
RS_p^s	1.00	3.19(±0.19)	1.78(±0.10)	0.60(±0.07)

Chlorination of 1-chlorobutane using t-butyl hypochlorite

The reaction was carried out at room temperature in carbon tetrachloride ((SOLVENT)/(SUBSTRATE) = 1.62). The reaction was initiated by a light from a 150w bulb.

(1-chlorobutane)/(t-butyl hypochlorite) ~ 10:1

	CH_3 —	CH_2 —	CH_2 —	CH_2Cl
% Distribution:	17.88	44.10	19.80	18.22
	15.52	43.14	21.86	19.48
	13.95	45.81	20.10	20.13
Mean:	15.78(±1.98)	44.35(±1.35)	20.59(±1.11)	19.28(±0.97)
$\frac{Kx}{K_4}$	1.00	2.84(±0.41)	1.32(±0.18)	1.24(±0.21)
RS_p^s	1.00	4.26(±0.62)	1.98(±0.28)	1.86(±0.32)

Chlorination of 1-chlorobutane using trichloro methane sulphonyl chloride

The reaction was carried out at 77°C and initiated by the addition of a small amount of benzoyl peroxide.

(1-chlorobutane)/(CCl_3SO_2Cl) = 20:1

	CH_3 -	CH_2 -	CH_2 -	CH_2Cl
% Distribution	12.14	51.71	17.85	18.31
	10.52	52.93	19.71	16.84
	9.53	53.61	18.19	18.67
	7.44	53.40	19.87	19.29
Mean	9.91 (±1.97)	52.91 (±0.85)	18.91 (±1.03)	18.28 (±1.04)
$\frac{Kx}{K_4}$	1.00	5.34 (±1.24)	1.91 (± 0.50)	1.85 (±0.49)
RS_p^s	1.00	8.01 (±1.85)	2.86 (±0.75)	2.77 (±0.74)

Liquid phase photochlorination of valeryl chloride

All reactions were carried out at room temperature, 20°C. The g.l.c. column used was a 12' glass column packed with 25% T.T.P. on 'Embacel' at 140°C.

Neat valeryl chloride

	CH_3 —	CH_2 —	CH_2 —	CH_2COCl
% Distribution:	30.14	45.82	22.53	1.51
	28.61	46.73	23.47	1.18
	26.75	48.01	23.19	2.04
	28.24	47.44	23.20	1.12
Mean:	28.44(±1.39)	47.00(±0.94)	23.10(±0.40)	1.46(±0.42)
$\frac{Kx}{K_5}$	1.00	1.65(±0.11)	0.81(±0.04)	0.05(±0.02)
RS_p^s	1.00	2.48(±0.17)	1.22(±0.06)	0.08(±0.03)

Solvent: Benzene
(SOLVENT)/(SUBSTRATE) = 5.34

	CH_3 —	CH_2 —	CH_2 —	CH_2COCl
% Distribution:	17.37	66.29	15.09	1.25
	16.15	68.09	15.52	0.24
	16.81	67.97	15.04	0.18
	16.53	69.13	14.14	0.20
Mean:	16.72(±0.51)	67.87(±1.18)	14.95(±0.58)	0.47(±0.52)
$\frac{Kx}{K_5}$	1.00	4.06(±0.18)	0.89(±0.05)	0.03(±0.03)
RS_p^s	1.00	6.09(±0.27)	1.34(±0.07)	0.04(±0.05)

Solvent: Carbon disulphide
(SOLVENT)/(SUBSTRATE) = 3.94

	CH_3 —	CH_2 —	CH_2 —	CH_2COCl
% Distribution:	16.65	66.31	16.56	0.50
	17.14	65.70	16.57	0.61
	16.24	66.66	16.43	0.67
	16.61	67.16	15.56	0.66
	16.34	66.25	16.86	0.55
Mean:	16.60(±0.35)	66.42(±0.54)	16.40(±0.49)	0.60(±0.07)
$\frac{Kx}{K_5}$	1.00	4.00(±0.11)	0.99(±0.04)	0.03(±0.01)
RS_p^s	1.00	6.00(±0.16)	1.48(±0.06)	0.05(±0.01)

Liquid phase photochlorination of hexanoyl chloride

All the reactions were carried out at 20°C. The g.l.c. column used was a 12' glass column packed with 25% T.T.P. on 'Embacel' at 145°C.

Neat hexanoyl chloride

	CH_3 —	CH_2 —	CH_2 —	CH_2 —	CH_2COCl
% Distribution:	22.23	33.46	29.62	14.17	0.53
	25.06	33.23	27.92	13.59	0.20
	27.62	31.33	27.59	12.99	0.47
Mean:	24.97(±2.70)	32.67(±1.17)	28.38(±1.09)	13.58(±0.59)	0.40(±0.15)
$\frac{Kx}{K_6}$	1.00	1.31(±0.19)	1.13(±0.17)	0.55(±0.09)	0.01(±0.01)
RS_p^s	1.00	1.96(±0.28)	1.70(±0.25)	0.82(±0.13)	0.02(±0.01)

Solvent: Benzene

(SOLVENT)/(SUBSTRATE) = 7.77

	CH_3 —	CH_2 —	CH_2 —	CH_2 —	CH_2COCl
% Distribution:	11.88	45.06	33.67	9.39	--
	10.28	45.53	35.34	8.85	--
	10.06	46.59	34.76	8.60	--
Mean:	10.74(±0.99)	45.73(±0.78)	34.59(±0.85)	8.95(±0.40)	0.00
$\frac{Kx}{K_6}$	1.00	4.26(±0.44)	3.22(±0.35)	0.83(±0.04)	0.00
RS_p^s	1.00	6.39(±0.66)	4.83(±0.53)	1.25(±0.06)	0.00

Solvent: Carbon disulphide

(SOLVENT)/(SUBSTRATE) = 4.58

	CH_3 —	CH_2 —	CH_2 —	CH_2 —	CH_2COCl
% Distribution:	9.62	47.08	37.03	6.27	--
	9.19	48.99	35.97	5.86	--
	8.90	48.43	36.43	6.25	--
	9.55	48.43	36.26	5.76	--
	9.30	48.24	36.15	6.31	--
Mean:	9.31(±0.29)	48.23(±0.70)	36.37(±0.41)	6.09(±0.26)	0.00
$\frac{Kx}{K_6}$	1.00	5.18(±0.21)	3.91(±0.11)	0.65(±0.04)	0.00
RS_p^s	1.00	7.77(±0.32)	5.86(±0.16)	0.98(±0.06)	0.00

Liquid phase photochlorination of heptanoyl chloride

All the reactions were carried out at 20°C. The g.l.c. column was a 12' glass column packed with 25% T.T.P. on 'Embacel' at 150°C.

Neat heptanoyl chloride

	CH_3 —	CH_2 —	CH_2 —	CH_2 —	CH_2 —	CH_2COCl
% Distribution	17.73	29.99	27.09	18.06	7.33	0.29
	17.40	30.12	26.80	18.44	7.24	0.00
	17.06	29.46	27.26	17.94	7.64	0.64
	17.61	29.86	26.69	18.62	6.83	0.40
	17.59	29.83	26.96	18.35	6.82	0.45
Mean:	17.38(±0.24)	29.85(±0.25)	26.96(±0.23)	18.28(±0.28)	7.17(±0.35)	0.36(±0.24)
$\frac{Kx}{K_7}$	1.00	1.72(±0.02)	1.55(±0.03)	1.05(±0.01)	0.41(±0.03)	0.02(±0.01)
RS_p^s	1.00	2.58(±0.03)	2.33(±0.05)	1.58(±0.01)	0.62(±0.04)	0.03(±0.02)

Solvent: Benzene

(SOLVENT)/(SUBSTRATE) = 6.98

	CH_3 —	CH_2 —	CH_2 —	CH_2 —	CH_2 —	CH_2COCl
% Distribution:	4.63	37.59	35.55	18.78	3.45	--
	7.12	37.30	34.97	17.60	3.01	--
	7.70	37.60	33.72	17.69	3.29	--
	7.10	36.30	34.97	17.90	3.73	--
	7.36	37.27	34.13	17.72	3.52	--
Mean:	6.78(±1.23)	37.21(±0.53)	34.67(±0.73)	17.94(±0.48)	3.40(±0.27)	0.00
$\frac{Kx}{K_7}$	1.00	5.49(±1.37)	5.11(±1.34)	2.65(±0.73)	0.50(±0.13)	0.00
RS_p^s	1.00	8.23(±2.05)	7.67(±2.01)	3.97(±1.10)	0.75(±0.20)	0.00

Solvent: Carbon disulphide

(SOLVENT)/(SUBSTRATE) = 5.14

	CH_3 —	CH_2 —	CH_2 —	CH_2 —	CH_2 —	CH_2COCl
% Distribution:	6.13	35.34	36.50	19.61	2.42	--
	6.48	36.14	35.92	18.26	3.20	--
	6.41	36.14	34.90	19.06	3.49	--
	5.90	36.79	36.47	18.06	2.78	--
	6.32	35.34	36.61	19.08	2.65	--
Mean:	6.25(±0.23)	35.95(±0.62)	36.08(±0.71)	18.81(±0.64)	2.91(±0.43)	0.00
$\frac{Kx}{K_7}$	1.00	5.75(±0.27)	5.77(±0.30)	3.01(±0.14)	0.47(±0.06)	0.00
RS_p^s	1.00	8.63(±0.41)	8.66(±0.45)	4.51(±0.21)	0.70(±0.09)	0.00

Liquid phase photochlorination of valeronitrile

All reactions were carried out at 20°C. The g.l.c. column was a 12' glass column packed with 25% T.T.P. on 'Embacil' at 150°C.

Neat valeronitrile

	CH_3 —	CH_2 —	CH_2 —	CH_2CN
% Distribution:	31.34	45.45	18.64	4.57
	33.73	44.68	17.86	3.72
	31.65	46.87	16.62	4.86
Mean:	32.34(±1.30)	45.67(±1.11)	17.71(±1.02)	4.38(±0.59)
$\frac{Kx}{K_5}$	1.00	1.41(±0.08)	0.55(±0.04)	0.13(±0.02)
RS_p^s	1.00	2.12(±0.12)	0.82(±0.06)	0.20(±0.03

Solvent: Benzene
(SOLVENT)/(SUBSTRATE) = 4.67

	CH_3 —	CH_2 —	CH_2 —	CH_2CN
% Distribution:	23.96	61.92	14.12	0.00
	23.00	62.67	13.60	0.73
	21.91	63.38	13.81	0.00
Mean:	22.96(±1.03)	62.66(±0.73)	13.84(±0.66)	0.24(±0.42)
$\frac{Kx}{K_5}$	1.00	2.73(±0.15)	0.61(±0.03)	0.01(±0.02)
RS_p^s	1.00	4.10(±0.23)	0.91(±0.04)	0.02(±0.03)

Solvent: Carbon disulphide

(SOLVENT)/(SUBSTRATE) = 10.68

	CH_3 —	CH_2 —	CH_2 —	CH_2CN
% Distribution:	16.63	71.95	11.42	0.00
	14.96	70.47	14.01	0.56
	13.23	73.02	13.31	0.44
	12.74	72.43	13.63	1.20
	14.67	73.18	12.15	0.00
	16.31	70.40	12.27	1.02
	17.73	69.71	11.98	0.58
Mean:	15.18(±1.82)	71.59(±1.39)	12.68(±0.97)	0.54(±0.46)
$\frac{Kx}{K_5}$	1.00	4.78(±0.65)	0.85(±0.16)	0.05(±0.03)
RS_p^s	1.00	7.17(±0.98)	1.28(±0.24)	0.07(±0.05)

Liquid phase photochlorination of fluorobutane

All reactions were carried out at 20°C. The g.l.c. column was a 12' glass column packed with 25% T.T.P. on 'Embacel' at 90°C.

Solvent: 1,1,2-trichloro-1,2,2-trifluoroethane

(SOLVNET)/(SUBSTRATE) = 1.63

	CH_3 —	CH_2 —	CH_2 —	CH_2F
% Distribution:	31.48	40.30	18.65	9.57
	31.20	40.50	18.99	9.31
	32.52	39.03	18.77	9.68
Mean:	31.73(±0.70)	39.94(±0.80)	18.80(±0.17)	9.52(±0.12)
$\frac{kx}{K_4}$	1.00	1.27(±0.03)	0.59(±0.01)	0.30(±0.01)
RS_p^s	1.00	1.90(±0.05)	0.89(±0.02)	0.45(±0.01)

Solvent: Benzene

(SOLVENT)/(SUBSTRATE) = 4.40

	CH_3 —	CH_2 —	CH_2 —	CH_2F
% Distribution:	23.05	69.82	--	7.13
	29.91	69.96	--	6.13
	23.01	70.64	--	6.35
Mean:	23.32(±0.51)	70.14(±0.44)	--	6.54(±0.53)

(No 2-chloro-1-fluorobutane was observed because it has the same retention time on the g.l.c. chromatogram as benzene)

$\frac{Kx}{K_4}$	1.00	3.01(±0.07)	--	0.28(±0.03)
RS_p^s	1.00	4.51(±0.11)	--	0.42(±0.04)

Solvent: Carbon disulphide

(SOLVENT)/(SUBSTRATE) = 6.48

	CH_3 —	CH_2 —	CH_2 —	CH_2F
% Distribution	15.85	58.37	19.54	6.24
	16.53	63.16	14.61	5.70
	16.06	63.08	14.95	5.91
	18.49	62.97	14.72	4.12
Mean:	16.73(±1.21)	61.90(±2.35)	15.96(±2.39)	5.49(±0.94)
$\frac{Kx}{K_4}$	1.00	3.70(±0.12)	0.95(±0.19)	0.33(±0.07)
RS_p^s	1.00	5.55(±0.18)	1.43(±0.28)	0.49(±0.11)

Liquid phase photochlorination of 1,1,1-trifluoropentane

The reactions were carried out at 20°C. The g.l.c. analysis was carried out using a 6' glass column packed with 25% T.T.P. on 'Embacel' at 90°C.

Neat 1,1,1-trifluoropentane

	CH_3 —	CH_2 —	CH_2 —	CH_2CF_3
% Distribution:	30.95	51.99	16.71	0.35
	29.64	52.45	17.50	0.41
	30.52	53.25	16.20	0.03
	31.54	51.23	16.83	0.40
	30.83	51.54	17.17	0.46
Mean:	30.70(±0.70)	52.09(±0.79)	16.88(±0.49)	0.33(±0.17)
$\frac{Kx}{K_5}$	1.00	1.70(±0.06)	0.55(±0.02)	0.01(±0.01)
RS_p^s	1.00	2.55(±0.09)	0.83(±0.04)	0.02(±0.01)

Solvent: Chlorobenzene

(SOLVENT)/(SUBSTRATE) = 7.49

	CH_3 —	CH_2 —	CH_2 —	CH_2CF_3
% Distribution:	19.45	66.79	13.76	--
	21.29	65.83	12.88	--
	22.20	64.22	13.58	--
	19.42	66.16	14.42	--
	20.20	67.33	12.47	--
Mean:	20.51(±1.21)	66.07(±1.18)	13.42(±0.76)	--
$\frac{Kx}{K_5}$	1.00	3.23(±0.23)	0.66(±0.06)	0.00
RS_p^s	1.00	4.85(±0.35)	0.99(±0.10)	0.00

Solvent: Carbon disulphide

(SOLVENT)/(SUBSTRATE)

	CH_3 —	CH_2 —	CH_2 —	CH_2CF_3
% Distribution:	12.32	74.80	12.88	--
	10.62	78.16	11.22	--
	10.49	77.59	11.92	--
	11.37	76.69	11.94	--
	11.42	77.03	11.37	--
Mean:	11.24(±0.74)	76.85(±1.28)	11.87(±0.65)	0.00
$\frac{Kx}{K_5}$	1.00	6.86(±0.54)	1.06(±0.05)	0.00
RS_p^s	1.00	10.30(±0.82)	1.59(±0.08)	0.00

DISCUSSION

The chlorination of 1-chlorobutane

The gas phase photochlorination of 1-chlorobutane was undertaken primarily to see how the results obtained from the static system used here compared with those of Fredericks[36] who used a flow system. Table 9 shows the results:-

Table 9 RS_p^s for gas phase photochlorination of 1-chlorobutane

Temperature	CH_3 -- CH_2 -- CH_2 -- CH_2Cl (4) (3) (2) (1)				Ref.
60°C	1.00	4.12	2.19	0.68	This work
50°C	1.00	3.70	2.10	0.80	36

The results, considering the experimental error involved, are reasonably comparable. The only real discrepancy is at position (3), where the present study suggests that the gas phase reaction is a little more selective than was previously thought. The new value for position (3) is, in fact, in better accord with subsequent data. Probably the earlier work is in error because analysis was completed using thermal conductivity detectors for the g.l.c. and not a density balance as used in all subsequent work.

The results of the gas phase chlorination carried out over a temperature range (see Table 6) are too scattered to justify the calculation of Arrhenius parameters. However, the results in the liquid phase in both 'complexing' and 'non-complexing' media will yield Arrhenius parameters although the errors involved are considerable. The parameters are obtained by a least square treatment of the relative rate data and are summarised in Table 10.

Table 10 Relative Arrhenius parameters for the liquid phase chlorination of 1-chlorobutane

SOLVENT	E_4-E_3 (cal mol^{-1})	$(A_3)/(A_4)$	E_4-E_2 (cal mol^{-1})	$(A_2)/(A_4)$	E_4-E_1 (cal mol^{-1})	$(A_1)/(A_4)$
NEAT	593 (±127)	0.68 (±0.14)	8 (±93)	0.90 (±0.14)	-760 (±245)	0.94 (±0.39)
BENZENE	505 (±356)	1.42 (±0.89)	72 (±135)	1.05 (±0.23)	-519 (±8)	0.73 (±0.01)

The plot of relative data against $^{1}/T$ is shown in Figs. 9 & 10.

Although caution must be exercised before drawing too many conclusions from these figures, it would seem to be fairly safe to say that the increased selectivity in benzene is not solely due to an enthalpy effect. Table 11 shows the RS_p^s in both liquid phase reactions at 0^oC.

Table 11 RS_p^s for liquid phase chlorination of 1-chlorobutane at 0^oC

	CH_3 — (4)	CH_2 — (3)	CH_2 — (2)	CH_2Cl (1)
NEAT	1.00	3.09	1.37	0.36
BENZENE	1.00	5.29	1.77	0.42

The main difference is the greatly increased attack at position (3) when the reaction is carried out in benzene. The data in Table 10 shows similar differences in activation energy for both processes, but a much increased ratio of the pre exponential factors in benzene. This seems to be opposite to the situation in 1,1-dichloroethane (see Part One) where the increased selectivity in benzene was found to be a primarily enthalpy effect.

FIGURE 9 - Plot of $\ln(Kx/K_4)$ $10^3/T$ for neat liquid phase photochlorination of 1-chlorobutane

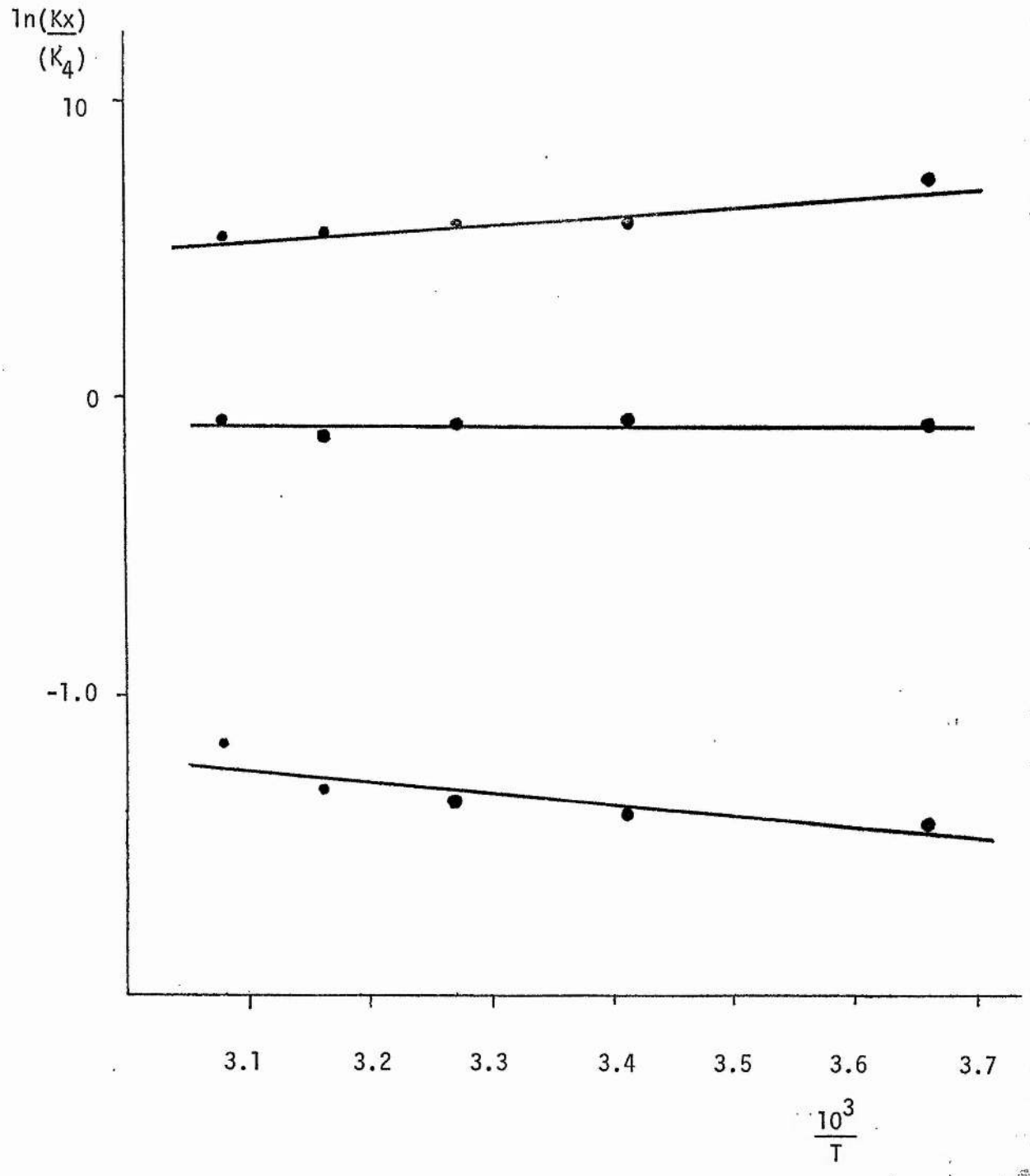
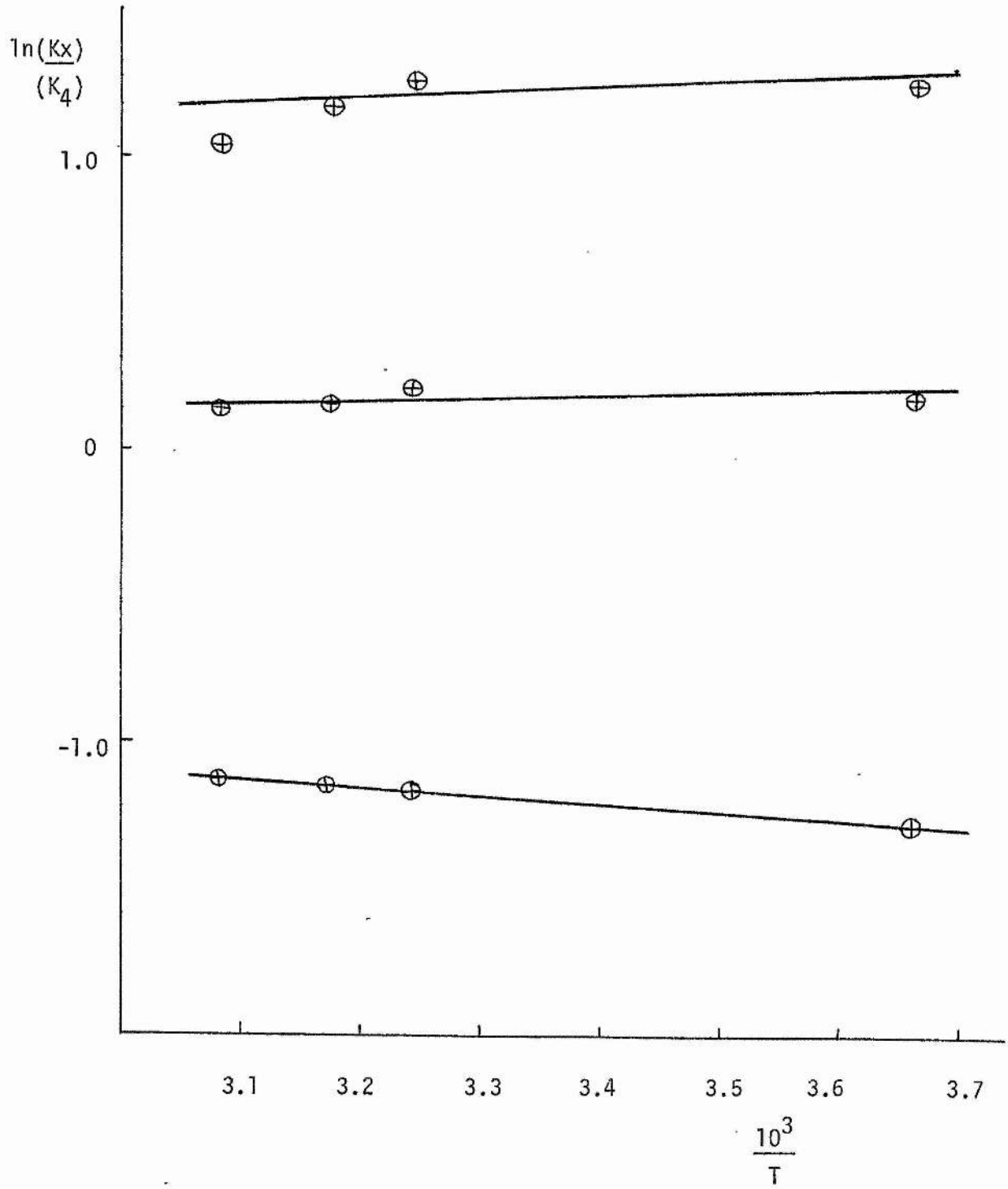


Figure 10 - Plot of $\ln(Kx/K_4)$ $10^3/T$ for the photochlorination of 1-chlorobutane in benzene



The increased attack at position (2) in benzene seems also to be mainly an entropy effect. However enthalpy effects may well prevail but are hidden because of the large experimental error involved. Even so, these results do add weight to Tedder's[17] argument that reaction selectivity is a balance of enthalpy and entropy effects.

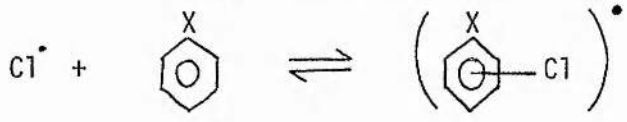
The effect of a range of solvents on the selectivity of the chlorination of 1-chlorobutane can be seen in Table 12.

Table 12 Selectivity for chlorination of 1-chlorobutane in various solvents

SOLVENT	(SOLVENT) / (1-CHLOROBUTANE)	RS_p^s CH_3 —	CH_2 —	CH_2 —	CH_2Cl
Acetyl Chloride	5.91	1.00	2.76	1.28	0.29
Carbon Tetra-chloride	3.96	1.00	2.23	1.20	0.30
Neat	--	1.00	2.68	1.38	0.36
$CF_2ClCFCl_2$	3.44	1.00	2.81	1.42	0.37
Nitrobenzene	4.08	1.00	3.47	1.65	0.25
Benzene	4.70	1.00	5.99	2.14	0.39
Carbon Disulphide	6.93	1.00	9.19	2.90	0.77
Perfluoro N-methyl Morpholine	5.65	1.00	3.19	1.78	0.60

Acetyl chloride does not seem to decrease the selectivity as it does with 1,1-dichloroethane. This adds weight to the argument that attack at position (1) in 1,1-dichloroethane is sterically hindered (see Part One). In 1-chlorobutane there is no real possibility of steric hinderance and so the selectivity in acetyl chloride is comparable with the neat liquid.

The reactions in 'complexing' solvents show increased attack at positions (2) and (3). Within experimental error, the attack at position (1) does not vary tremendously with solvent. Nitrobenzene does not increase the selectivity as much as benzene. This is probably due to the electron withdrawing effect of the nitro group on the aromatic nucleus. This is in agreement with the theory of π complex formation, the more electron rich an aromatic nucleus is the more likely it will form a 'π complex'.



Thus with nitrobenzene the above equilibrium will not be as far to the right as it will in benzene, so benzene is a more selective 'complexing' solvent. Russell[18] observed similar results when chlorinating 2,3-dimethylbutane. The selectivity in carbon disulphide is even higher than in benzene. This is due partly to the fact that it was used in a slightly higher concentration and so the equilibrium will be further to the right.

Unfortunately, a study of the chlorination of 1-chlorobutane in a wide variety of perfluorinated solvents could not be undertaken because it is immiscible in most of them. However, 1-chlorobutane was miscible with perfluoro-N-methyl morpholine. The chlorination in this solvent yielded a selectivity half way between neat liquid phase and gas phase. This is similar to the selectivities obtained with 1,1-dichloroethane (see Part One) and adds further weight to the argument that the inert perfluorosolvent breaks up the solvation of reactants and mimics gas phase conditions in the liquid phase.

Table 13 shows the selectivities for chlorination of 1-chlorobutane by various reagents in the liquid phase. The figures show that some reagents are more selective than chlorine.

Table 13 Relative selectivities of chlorination of 1-chlorobutane with various reagents

REAGENT	RADICAL	RS_p^s $CH_3 - CH_2 - CH_2 - CH_2Cl$				REFERENCE
Cl_2, 20°C (neat)	$Cl^{\bullet}$	1.00	2.68	1.38	0.37	This work
SO_2Cl_2, 80°C (neat)	$SO_2Cl^{\bullet}$	1.00	2.93	1.37	0.44	38
C_6H_5ICl, 40°C (neat)	$C_6H_5ICl^{\bullet}$	1.00	7.57	2.62	0.61	42
Bu^tOCl, 20°C (CCl_4)	$Bu^tO^{\bullet}$	1.00	4.26	1.98	1.86	This work (cf. 40)
CCl_3SO_2CL, 77°C (neat)	$CCl_3SO_2^{\bullet}$	1.00	8.01	2.86	2.77	This work
Cl_2O, 40°C (CCl_4)	$ClO^{\bullet}$	1.00	8.86	3.31	3.77	52

t-Butyl hypochlorite, trichloromethyl sulphonyl chloride and chlorine monoxide give considerably more attack at position (1). Walling[40] concluded that the t-butoxy radical is more sensitive to resonance effects than the chlorine atom but exhibits similar polar properties.

Perhaps a better way of explaining the higher selectivity using these radicals is that they have a higher α value than the chlorine atom in the Evans-Polyani[12] relationship. In other words, with these radicals bond strengths are more important than polar effects, and these have more say in determining the selectivity. The hydrogen abstraction reactions with these radicals will be more endothermic than abstraction by chlorine atoms and so, by the Hammond[13] postulate, bond strength must play a more important role, because there is more bond breaking in the transition state. It is also interesting to compare the selectivity using sulphuryl chloride and trichloromethyl sulphonyl chloride. The two abstracting radicals differ only in that one has the more powerfully electron withdrawing - CCl_3 - group attached. This seems to be enough to lower the reactivity of the radical and give a much more selective process.

The chlorination of 1-substituted butanes

The results for the liquid phase chlorination of some 1-substituted butanes in non-complexing media are shown in Table 14. Also included is the selectivity for the chlorination of 1-nitrobutane (see Part Four).

Table 14 Relative selectivities for the liquid phase chlorination of various 1-substituted butanes at 20°C

SOLVENT	$\overset{\delta}{CH_3}$ — $\overset{\gamma}{CH_2}$ — $\overset{\beta}{CH_2}$ — $\overset{\alpha}{CH_2}$ — X					Ref.
CCl_4	1.00	2.95	2.95	1.00	-H	16
Neat	1.00	2.68	1.38	0.36	-Cl	This work
Neat	1.00	2.55	0.83	0.02	$-CF_3$	" "
$CF_2Cl\ CFCl_2$	1.00	1.90	0.89	0.45	-F	" "
Neat	1.00	2.17	0.84	0.16	-CN	" "
Neat	1.00	2.48	1.22	0.08	-COCl	" "
CCl_4	1.00	2.31	0.37	0.01	$-NO_2$	Part 4

When the results in Table 14 are compared with the gas phase results (Table 5), one thing is immediately apparent; the selectivities as compared to n-butane show that the inductive effect deactivates the position γ as well as α and β to the substituent. This is in keeping with the observations of Singh and Tedder.[23,46] The results should be treated with a certain amount of caution when comparing with that for n-butane because in all probability in the liquid phase the deactivating effect of the substituent extends to position δ. However, analogies with the gas phase data are apparent. In the gas phase the substituents which most deactivate the β position are $-NO_2 > -CF_3 > -CN \sim -F$. (For the gas phase results of 1-nitrobutane see Part Four) This same trend also exists in liquid phase chlorination.

The reactivity of the α position is a balance between the deactivating polar inductive effect and the activating resonance stabilization of the incipient radical. Comparing gas and liquid phase data resonance stabilization appears to be less important in the liquid phase. It is most apparent in 1-chlorobutane and 1-fluorobutane. Attack at the α position where -CN, -COCl and $-NO_2$ are the substituents is very low and so there must be very little resonance stabilization in these cases. When $-CF_3$ is the substituent there is very little attack at the α position, but no resonance stabilization would be anticipated in this case anyway.

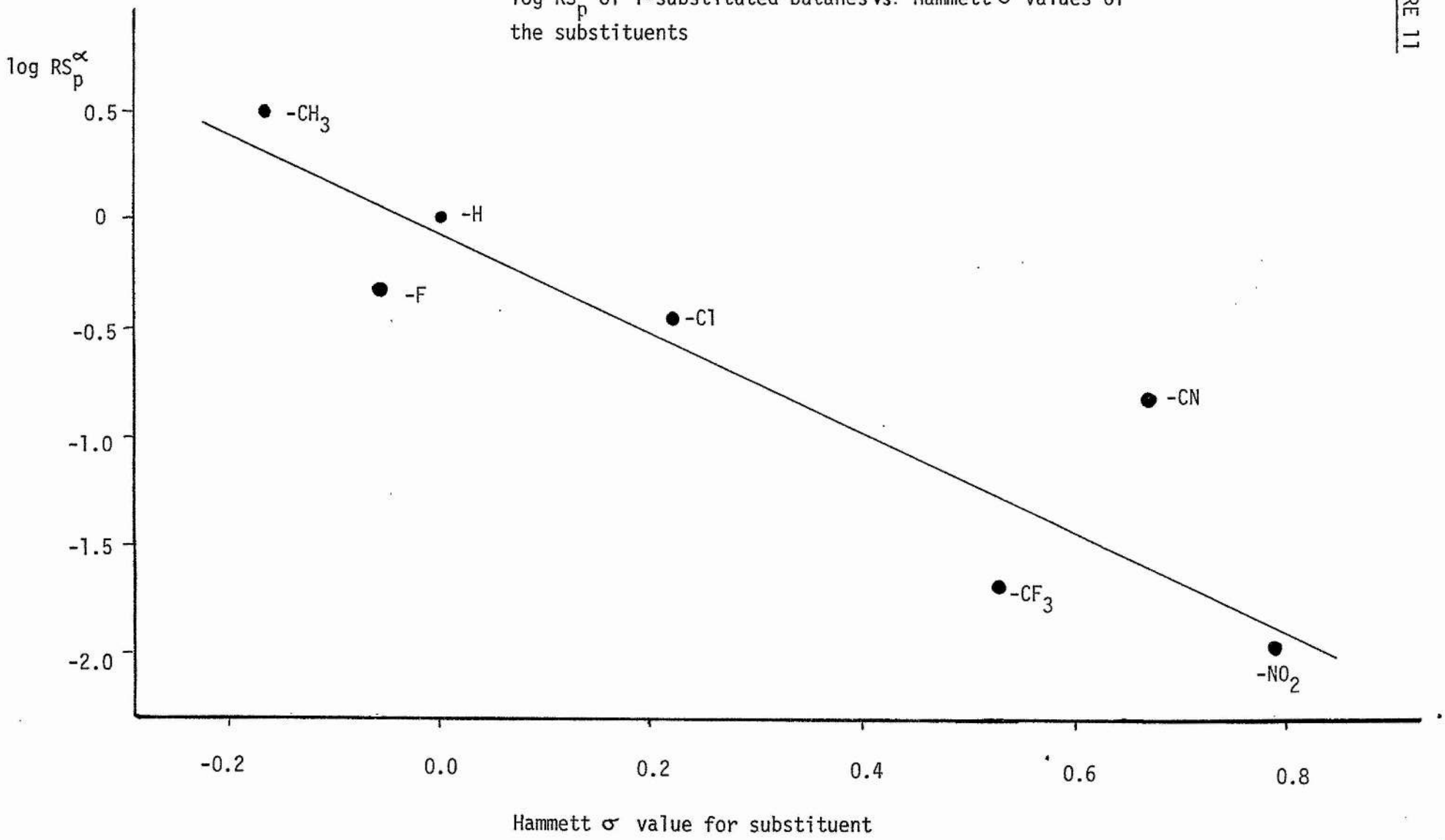

log RS_p^{α} of 1-substituted butanes vs. Hammett σ values of the substituents
log RS_p^{α}
0.5
0
-0.5
-1.0
-1.5
-2.0
-CH_3
-H
-F
-Cl
-CN
-CF_3
-NO_2
-0.2
0.0
0.2
0.4
0.6
0.8
Hammett σ value for substituent

FIGURE 11

Table 15 RS_p^s values for chlorination of 1-substituted butanes in Benzene

SOLVENT CONC.	RS_p^s CH_3 — CH_2 — CH_2 — CH_2 - X (δ) (γ) (β) (α)					REFERENCE
9M, 68°	1.00	5.11	5.11	1.00	H	16
3.8M	1.00	5.99	2.14	0.39	Cl	This work
4.4M	* 1.00	4.51	--	0.42	F	" "
7.5M	+ 1.00	4.85	0.99	0.00	CF_3	" "
4.67M	1.00	4.10	0.91	0.02	CN	" "
5.34M	1.00	6.09	1.34	0.04	COCl	" "
7.20M	1.00	4.82	0.44	0.00	NO_2	Part 4

(+ This reaction was done in chlorobenzene because benzene obscured two of the products in the g.l.c. analysis)

(* No attack at position 2 was determined because the solvent obscured the product in the g.l.c. analysis)

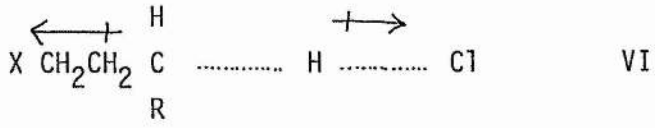
Table 16 RS_p^s values for chlorination of 1-substituted butanes in carbon disulphide

SOLVENT CONC.	RS_p^s CH_3 — CH_2 — CH_2 — CH_2 - X (δ) (γ) (β) (α)					REFERENCE
11.2M	1.00	9.93	9.93	1.00	H	16
3.8M	1.00	9.16	2.89	0.77	Cl	This work
6.5M	1.00	5.55	1.43	0.49	F	" "
12.6M	1.00	10.30	1.59	0.00	CF_3	" "
10.7M	1.00	7.17	1.28	0.07	CN	" "
4.0M	1.00	6.00	1.48	0.05	COCl	" "

The analogy can be drawn with the effects of a substituent on a benzene ring. For example, a chlorine atom attached to a benzene ring withdraws electrons by it's inductive effect, and donates them by a resonance effect. This is similar to the activation and deactivation of the α position in 1-substituted butanes by inductive and resonance effects. Fig. 11 shows a rough correlation between log RS_p^{α} and the Hammett σ^{-66} values for the para position of the equivalent aromatic compound. The ρ value (i.e. the slope of the graph) is negative, and this is reasonable for a reaction involving electron demand. A better correlation cannot really be expected, because the Hammett σ values are obtained for studies on quite different systems. However, it does give further support to the argument that inductive and resonance effects in atomic chlorination of substituted alkanes and the effects of substituents on aromatic reactivity are analogous.

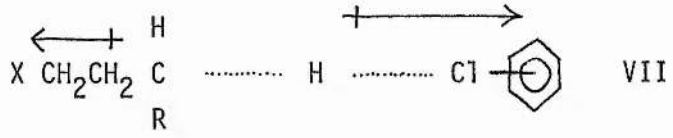
Tables 15 and 16 show the effects of complexing solvents on the relative selectivities in the series of 1-substituted butanes. As expected the selectivities are much higher than those in the neat liquid phase reactions. Assuming that selectivity does not vary too much with complexing solvent concentration once a certain level has been reached (the chlorination of 1,1-dichloroethane over a benzene concentration range done in Part One seems to indicate this) one or two conclusions may be drawn from this data. The deactivating polar inductive effect still seems to be apparent with some substituents. Attack at position γ in the cases where -F, $-NO_2$, $-CF_3$ and -CN are the substituents seems to be slightly less in the unsubstituted butane. However, when the substituent is -Cl, and in benzene -COCl, attack at position γ is increased i.e. the deactivating effect is not as strong. Thus in a complexing solvent the repulsive effects are lessened the further away the hydrogen atom is from the substituent. This may be compared to the neat liquid phase situation diagramatically:-

Neat liquid:



VI

Complexing solvent:



VII

The strength of the dipole moment set up during the abstraction process in the complexing solvent would be less than that of an uncomplexed chlorine atom. Therefore, the repulsive effect with the dipole due to the substituent would be less in a complexing solvent and this must lead to greater reactivity. The lower reactivity of the terminal hydrogens may be due to the lowering of overall starting energy of the reactants by the complexing solvent. This would cause a greater difference in activation energy between primary and secondary hydrogen abstraction and help towards increasing the selectivity.

Further evidence that the deactivating effect of an electron withdrawing substituent is transmitted further along the chain than in the gas phase can be found in Tables 17, 18 and 19.

Table 17 $\underline{RS_p^s \text{ values for the chlorination of long chain acid chlorides in the liquid phase}}$

C —	C —	C —	C —	C —	C —	COCl
		1.00	2.48	1.22	0.08	
	1.00	1.78	1.54	0.79	0.03	
1.00	2.53	2.33	1.56	0.61	0.03	

Table 18 RS_p^s values for the chlorination of long chain acid chlorides in benzene

SOLVENT CONC.	C —	C —	C —	C —	C —	C —	COCl
5.34			1.00	6.09	1.34	0.04	
7.77		1.00	6.39	4.83	1.25	0.00	
6.98	1.00	5.23	7.67	3.97	0.75	0.00	

Table 19 RS_p^s values for the chlorination of long chain acid chlorides in carbon disulphide

SOLVENT CONC.	C —	C —	C —	C —	C —	C —	COCl
3.94			1.00	6.00	1.48	0.05	
4.58		1.00	7.77	5.86	0.98	0.00	
5.14	1.00	8.63	8.66	4.51	0.70	0.00	

The selectivities for the chlorination of acid chlorides neat in the liquid phase does show increasing selectivity along the length of the carbon chain. Singh and Tedder[23] have attributed the effect of the substituent beyond the β position to facilitated charge separation in the transition state. The selectivity does seem to reach a constant value at the δ and ϵ carbon atoms in heptanoyl chloride.

Similarly, in complexing solvents, the inductive influence can be seen up to the carbon atoms δ and ϵ from the substituent. However, the increased selectivity in these solvents can probably be attributed to the decreased repulsive effects in the transition states shown in VI and VII, the deactivating effect of the substituent becomes less and less along the chain and in both benzene and carbon disulphide similar selectivities are found at the δ and ϵ atoms in heptanoyl chloride.

PART THREE

The Chlorination of 1,4-Disubstituted Butanes

PART THREE

Introduction

The Chlorination of 1,4-Disubstituted Butanes

This work was undertaken to see how the substituents at each end of a butane chain affect the distribution of chlorinated products. Tedder[23,46] has proposed that in gas phase halogenation, the inductive effect of the substituent has no influence beyond the β position. This being the case, gas phase chlorination of a 1,4-disubstituted butane ought to give a ratio of the α and β chloro products similar to the ratio found in the respective 1-substituted butane.

Chlorination of 1,4-disubstituted butanes in the liquid phase ought to yield more information about the influence of the inductive effect of a substituent along an alkane chain.

Very little work seems to have been done on the chlorination of 1,4-disubstituted butanes. Horner and Schlafer[39] chlorinated 1,4-dichlorobutane but only appeared to detect one product: 1,2,4-trichlorobutane. In a series of competitive chlorinations using t-butyl hypochlorite Migita et al[54] chlorinated 1,4-dichlorobutane but give no information about the product distribution.

As well as 1,4-dichlorobutane, the chlorination of 1,4-difluorobutane, 1-chloro-4-fluoro-butane and 5-chlorovaleryl chloride were studied. The chlorination of these compounds does not appear to have been studied previously.

Experimental

Materials

Chlorine was used as supplied by British Oxygen Company. 1,4-dichlorobutane (B.D.H.) was purified by distillation and the purity checked by gas liquid chromatography. 5-chloro valeryl chloride (Aldrich) was used as supplied. Again all solvents were used as supplied by the manufacturers. 1,4-difluorobutane and 1-chloro-1-fluorobutane were synthesised. 1-fluorobutane was synthesised as described in Part 2.

Preparation of 1,4-difluorobutane[55]

Redistilled ethylene glycol (300ml) was placed in a 500ml round bottomed three necked flask along with anhydrous potassium fluoride (2.5 moles, 145g). A stirrer, dropping funnel and distillation column were attached to the three necked flask. The contents were heated to 160°c then 1,4-dichlorobutane (1 mole, 111ml) added slowly. The product formed almost immediately, and was collected into a 50ml round bottomed flask from the distillation column. The 1,4-difluorobutane was further purified by preparative gas liquid chromatography using a 12' glass column packed with 25% tritolyl phosphate on 'Embacel' at 110°c,

1,4-difluorobutane:

n.m.r. δ = 1.6 and 1.9 (doublet of multiplets, J_{H-F} = 24 Hz, 4H, $FCH_2\underline{CH_2}\underline{CH_2}CH_2F$)

δ = 4.2 and 4.8 (doublet of triplets, J_{H-F} = 48Hz, J_{H-H} = 12Hz 4H, $F\underline{CH_2}CH_2CH_2\underline{CH_2}F$)

Preparation of 1-chloro-4-fluorobutane[56]

Redistilled Dimethyl formamide (300ml) was placed in a 500ml round bottomed three necked flask along with anydrous potassium fluoride (2 moles, 116g). A stirrer, dropping funnel and condenser were attached to the three necked flask. The contents were heated to 130°c and then 1,4-dichlorobutane (1 mole, 111ml) added slowly. The mixture was stirred for several hours. The product was extracted from the dimethyl formamide by the addition of water. It was then extracted with ether, dried and purified by preparative gas liquid chromatography. The column was 12' glass packed with 25% tritolyl phosphate on 'Embacel' at 120°c.

1-chloro-4-fluorobutane

n.m.r. = 1.5-2.1 (complex, 4H, $FCH_2\underline{CH_2}\underline{CH_2}CH_2Cl$)
= 3.6 (triplet, J = 10Hz, 2H, $FCH_2CH_2CH_2\underline{CH_2}Cl$)
= 4.2 and 4.7 (doublet of triplets, J_{H-F} = 4.6Hz, J_{H-H} = 10Hz, 2H, $F\underline{CH_2}CH_2CH_2CH_2Cl$)

Apparatus and Procedure

Gas Phase Reactions: Gas phase experiments were carried out on the same static system described in Part One. The procedure was essentially the same except that i) lower reaction pressures were used due to the low volatility of the reactants, ii) the products were collected using the apparatus depicted in Fig. 12. A small collecting tube was blown at the bottom of the reaction vessel. At the end of the reaction this was immersed in liquid nitrogen and the products given time to condense. The bottom manifold of the vacuum line (see Fig.12) was filled with nitrogen. This was then added to the reaction vessel and the pressure raised. The process was repeated until the pressure inside the reaction vessel was about equal to atmospheric pressure. The vessel was then removed from the line and the sample tube cut off and stored. The mixture was then analysed by gas liquid chromatography.

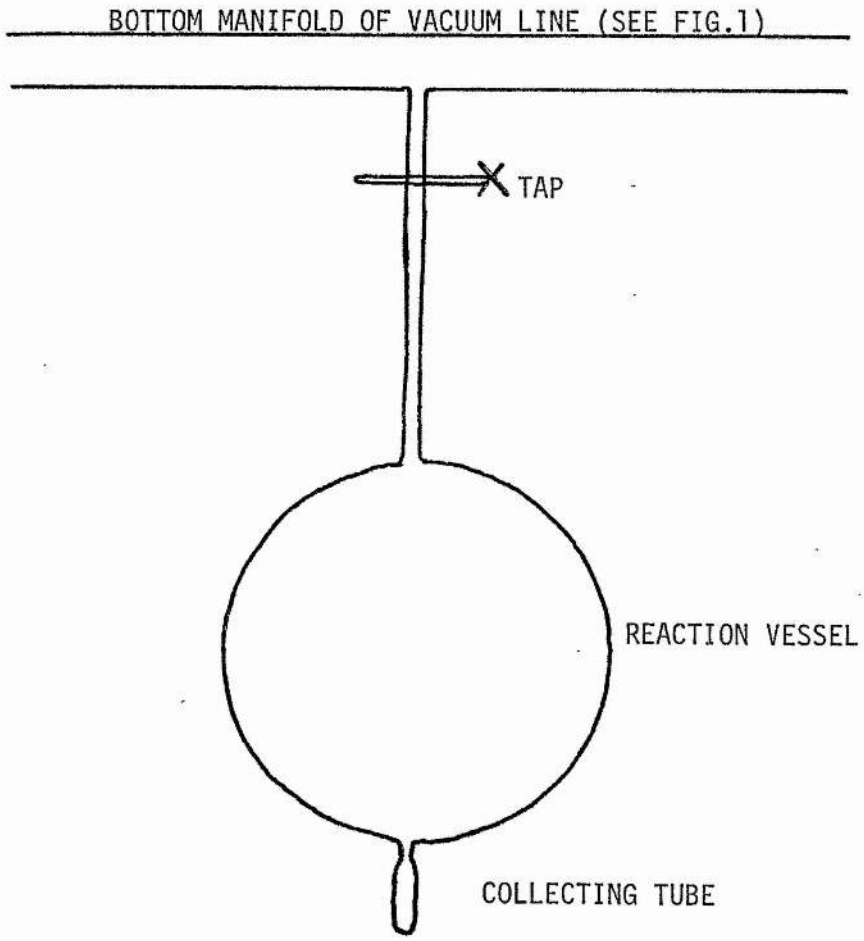

BOTTOM MANIFOLD OF VACUUM LINE (SEE FIG.1)
TAP
REACTION VESSEL
COLLECTING TUBE

FIGURE 12

Liquid Phase Reactions: All reactions in the liquid phase were carried out in the same way as described in Part One.

Analysis of the Products

The products of all the reactions were analysed by gas liquid chromatography (see Part One). Three types of column were used: a 6' glass column packed with 25% tritolyl phosphate (T.T.P.) on 80/100 mesh 'Embacel', a 12' glass column packed with 25% T.T.P. on 80/100 mesh 'Embacel' and a 10' glass column packed with 40% T.T.P. on 80/100 mesh 'Chromasorb'.

The products of the chlorination of 1,4-dichlorobutane were assumed to elute in the order 1,1,4-trichlorobutane and 1,2,4-trichlorobutane. This was based on their boiling points: $CH_2(Cl)CH_2CH(Cl)CH_2Cl$ ($B.p._{10} = 63^oC$)[57] and $CH_2(Cl)CH_2CH_2CHCl_2$ ($B.p._{760} = 184^oC$)[38,57]

As no information could be found on the products of the chlorination of 1,4-difluorobutane their identities were determined by preparative gas liquid chromatography using a 6' column packed with 25% tritolyl phosphate at 110°c followed by n.m.r. spectoscopy.

1-chloro-1,4-difluorobutane:

n.m.r. δ = 1.7-2.5 (complex, 4H, $FCH_2\underline{CH_2}\underline{CH_2}CHClF$)
δ = 4.3 and 4.8 (doublet of triplets, J_{H-F}= 46Hz J_{H-H}= 12Hz 2H, $F\underline{CH_2}CH_2CH_2CHClF$)
δ = 5.9 and 6.6 (doublet of triplets, H_{H-F}=50Hz J_{H-H}= 10Hz 1H, $FCH_2CH_2CH_2\underline{CH}ClF$)

2-chloro-1,4-difluorobutane:

n.m.r. δ = 2.1-2.9 (complex 3H, $FCH_2\underline{CH_2}\underline{CH}(Cl)CH_2F$)
δ = 4.1-4.5 and 4.8-5.1 (complex 4H, $F\underline{CH_2}\underline{CH_2}CH(Cl)CH_2F$)

The elution order was established as 1-chloro-1,4-difluorobutane and 2-chloro-1,4-difluorobutane.

The products of the chlorination of 1-chloro-4-fluorobutane could not be resolved properly so no attempt was made to identify them. It was assumed that the elution order would be 1,1-dichloro-4-fluoro-, 1,2-dichloro-4-fluoro, 1,3-dichloro-4- fluoro, and 1,4-dichloro-4-fluoro. The last three isomers could not be resolved by any of the columns used.

The products of the chlorination of 5-chlorovaleryl chloride were identified by both preparative gas liquid chromatography /n.m.r. spectroscopy and synthesis. The esters of the reaction products were formed by the addition of methanol. This made separation by g.l.c. easier. Prep. g.l.c. gave the 5,5-dichloro isomer and a mixture of the 3,5- and 4,5-dichloroisomers. The 2,5-dichloroisomer was formed in small quantities and could not be isolated.

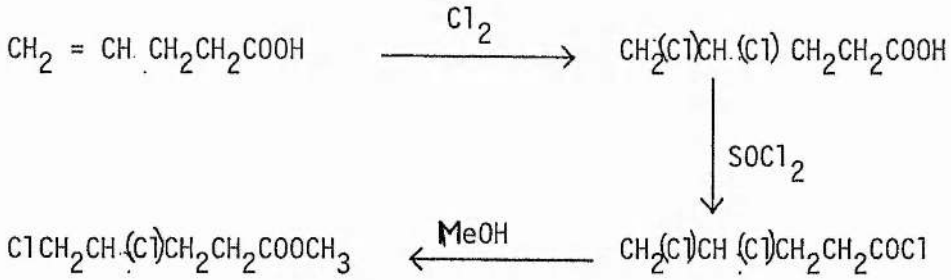
Methyl-5,5-dichlorovalerate

n.m.r. δ = 1.7-2.5 (complex 6H, $Cl_2CH\underline{CH_2}\underline{CH_2}\underline{CH_2}COOCH_3$)
δ = 3.7 (singlet, 3H, $Cl_2CHCH_2CH_2CH_2COO\underline{CH_3}$)
δ = 6.8(triplet, J = 10Hz, 1H, $Cl_2\underline{CH}CH_2CH_2CH_2COOCH_3$)

Methyl-4,5-dichlorovalerate and methyl-3,5-dichlorovalerate

n.m.r. δ = 1.8-2.6 (complex, 4H, $ClCH_2CH(Cl)\underline{CH_2}CH_2COOCH_3$
$ClCH_2\underline{CH_2}CH(Cl)CH_2COOCH_3$)
δ = 2.5 (triplet, 2H, $ClCH_2CH(Cl)CH_2\underline{CH_2}COOCH_3$)
δ = 3.8 (Doublet, 2H, $ClCH_2CH_2CH(Cl)\underline{CH_2}COOCH_3$)
δ = 3.6-3.9 (complex, 10H, $Cl\underline{CH_2}CH(Cl)CH_2CH_2COO\underline{CH_3}$
$Cl\underline{CH_2}CH_2CH)Cl)CH_2COO\underline{CH_3}$)
δ = 4.0-4.3 (complex, 1H, $ClCH_2CH_2\underline{CH}(Cl)CH_2COOCH_3$)
δ = 4.4-4.7 (complex, 1H, $ClCH_2\underline{CH}(Cl)CH_2CH_2COOCH_3$)

To distinguish between the 3,5 and 4,5-dichloroisomers the methyl ester of 4,5-dichlorovaleric acid was synthesised. Allyl propionic acid (Fluka) was reacted with chlorine gas for a short time in the dark. The mixture was then distilled under reflux with thionyl chloride (B.D.H.) for about one hour. The excess thionyl chloride was distilled off and the residual acid chloride was reacted with excess methanol. The mixture was then analysed by g.l.c. using a 12' glass column packed with 25% T.T.P. at 150°c. This column could separate the 3,5 and 4,5-dichloroisomers after about four hours elution time. Although the synthetic mixture was quite impure a peak appeared with the same retention time as one of the dichloro isomers from a reaction mixture and this peak was therefore assigned as that of the methyl ester of 4,5-dichloro valeric acid.



Using a shorter column a fourth peak could be assigned. This was assumed to be the methyl ester of 2,5-dichlorovaleric acid. A 6' glass column packed with 25% T.T.P. on Embacel at 150°c was used to determine the distribution of the 2,5- and 5,5-dichloroisomers. A 12' glass column packed with 25% T.T.P. on 'Embacel' was used to determine the distribution of the 3,5-,4,5- and 5,5-dichloro isomers.

RESULTS

Chlorination of 1,4-dichlorobutane

Gas Phase: Temperature: 120°c
Column: 12' 25% T.T.P. on 'Embacel' at 150°c

	(Cl — CH_2 —	CH_2 —)$_2$
% Distribution:	33.14	66.86
	34.15	65.85
	34.64	65.36
	34.50	65.50
	33.32	66.68
Mean:	33.95(±0.68)	66.05(±0.68)
RS_1^2	1.00	1.95(±0.06)

Liquid Phase: Temperature: 20°c
Column: 12' 25% T.T.P. on 'Embacel' at 150°c

	(Cl — CH_2 —	CH_2 —)$_2$
% Distribution:	28.22	71.78
	28.32	71.68
	31.83	68.17
	29.82	70.18
	28.30	71.70
Mean:	29.30(±1.57)	70.70(±1.57)
RS_1^2	1.00	2.42(±0.17)

Benzene: Temperature: 20°c
Column: 12' 25% T.T.P. on 'Embacel' at 150°c
(SOLVENT) / (SUBSTRATE) = 3.98

	(Cl — CH_2 —	CH_2 —)$_2$
% Distribution:	32.86	67.14
	32.55	67.45
	33.49	66.51
	32.41	67.59
Mean:	32.83(±0.48)	67.17(±0.48)
RS_1^2	1.00	2.05(±0.04)

Chlorination of 1,4-difluorobutane

Gas Phase: Temperature: 115°c
Column: 6' 25% T.T.P. on 'Embacel' at 110°c

	(F — CH_2 —	CH_2 —)$_2$
% Distribution:	41.24	58.76
	42.71	57.29
	44.66	55.34
	42.86	57.14
	42.68	57.32
Mean:	42.83(±1.22)	57.17(±1.22)
RS_1^2	1.00	1.34(±0.07)

Liquid Phase: Temperature: 20°c
Column: 6' 25% T.T.P. on 'Embacel' at 110°c

	(F — CH_2 —	CH_2 —)$_2$
% Distribution:	38.23	61.77
	39.18	60.82
	38.40	61.60
	39.14	60.86
	38.59	61.41
Mean:	38.71(±0.43)	61.29(±0.43)
RS_1^2	1.00	1.58(±0.03)

Benzene: Temperature: 20°c
Column: 6' 25% T.T.P. on 'Embacel' at 110°c
(SOLVENT) / (SUBSTRATE) = 3.72

	(F — CH_2 —	CH_2 —)$_2$
% Distribution	45.83	54.17
	44.97	55.03
	44.41	55.59
	41.17	58.83
	43.75	56.25

Mean:	44.03(±1.77)	55.97(±1.77)
RS_1^2	1.00	1.27(±0.09)

Gas Phase Chlorination of 1-fluorobutane

Temperature: 115°c
Column: 12' 25% T.T.P. on 'Embacel' at 110°c

	CH_3 —	CH_2 —	CH_2 —	CH_2F
% Distribution:	20.84	45.63	21.12	12.42
	20.59	45.57	20.11	13.73
	22.32	45.87	21.08	10.74
	21.35	45.76	21.45	11.44
Mean:	21.28(±0.77)	45.71(±0.13)	20.94(±0.58)	12.08(±1.30)
RS_p^s	1.00	3.23(±0.10)	1.48(±0.05)	0.85(±0.11)

Gas Phase chlorination of 1-chloro-4-fluorobutane

Temperature: 115°c
Columns: 12' 25% T.T.P. on 'Embacel' at 120°c
10' 40% T.T.P. on 'Chromasorb' at 145°c
10' 40% T.T.P. on 'Chromasorb' at 120°c

	Cl —	CH_2 —	CH_2 —	CH_2 —	CH_2 — F
% Distribution:		19.35		80.65	
		16.79		83.21	
		17.62		82.38	
Mean:		17.92(±1.31)		82.08(±1.31)	

Chlorination of 5-chlorovaleryl chloride

Gas Phase: Temperature: 130°c
Column: 6' 25% T.T.P. on 'Embacel' at 150°c

	Cl —	CH_2 —	CH_2 —	CH_2 —	CH_2COCl
% Distribution:		86.10	--	--	13.90
		85.78	--	--	14.22
		85.10	--	--	14.90
Mean:		85.66(±0.51)			14.34(±0.51)

Column: 12' 25% T.T.P. on 'Embacel' at 140°c

	Cl —	CH_2 —	CH_2 —	CH_2 —	CH_2COCl
% Distribution:		17.77	39.67	42.56	--
		21.64	39.09	39.27	--
		19.94	39.80	40.26	--
Mean:		19.78(±1.94)	39.52(±0.38)	40.70(±1.69)	

Total % Distribution:

	Cl —	CH_2 —	CH_2 —	CH_2 —	CH_2COCl
		19.15	38.25	39.40	3.20
RS_5^X		1.00	2.00	2.06	0.17

Liquid Phase: Solvent: Carbon Tetrachloride (SOLVENT)/(SUBSTRATE)=6.67
Temperature: 20°c
Column: 6' 25% T.T.P. on 'Embacel' at 150°c

	Cl —	CH_2 —	CH_2 —	CH_2 —	CH_2COCl
% Distribution:		84.77	--	--	15.23
		82.10	--	--	17.90
		89.94	--	--	16.06
		87.34	--	--	12.66
Mean:		84.54(±2.18)	--	--	15.46(±2.18)

Column: 12' 25% T.T.P. on 'Embacel' at 140°c

	Cl —	CH_2 —	CH_2 —	CH_2 —	CH_2-COCl
% Distribution:		32.55	48.82	18.63	--
		36.04	44.59	19.37	--
		31.92	48.38	19.70	--
		36.44	46.20	17.36	--
		32.30	48.33	19.37	--
Mean:		33.85(±2.20)	47.26(±1.81)	18.89(±0.94)	

Total % Distribution:

	Cl —	CH_2 —	CH_2 —	CH_2 —	CH_2COCl
		31.88	44.51	17.79	5.82
RS_5^x		1.00	1.40	0.56	0.18

Solvent: Benzene
Temperature: 20°c (SOLVENT)/(SUBSTRATE) = 7.29
Column: 6' 25% T.T.P. on 'Embacel' at 150°c

	Cl —	CH_2 —	CH_2 —	CH_2 —	CH_2COCl
% Distribution:		94.51	--	--	5.49
		94.69	--	--	5.31
		96.86	--	--	3.14
		95.35	--	--	4.65
Mean:		95.35(±1.07)			4.65(±1.07)

Column: 12' 25% T.T.P. on 'Embacel' at 140°c

	Cl —	CH_2 —	CH_2 —	CH_2 —	CH_2COCl
% Distribution:		21.84	47.83	30.33	--
		21.51	45.10	33.39	--
		19.72	47.21	33.00	--
		22.48	44.92	32.60	--
Mean:		21.39(±1.18)	46.27(±1.47)	32.33(±1.37)	

Total % Distribution:

Cl —	CH_2 —	CH_2 —	CH_2 —	CH_2COCl
	21.17	45.80	32.00	1.03
RS_5^x	1.00	2.16	1.51	0.05

Solvent: Carbon disulphide
Temperature: 20°c
(SOLVENT)/(SUBSTRATE) = 10.71
Column: 6' 25% T.T.P. on 'Embacel' at 150°c

Cl —	CH_2 —	CH_2 —	CH_2 —	CH_2COCl
% Distribution:	94.15	--	--	5.85
	93.13	--	--	6.87
	93.33	--	--	6.67
	91.49	--	--	8.51
	92.40	--	--	7.60
Mean:	92.90(±1.00)			7.10(±1.00)

Column: 12' 25% T.T.P. on 'Embacel' at 140°c

Cl —	CH_2 —	CH_2 —	CH_2 —	CH_2COCl
% Distribution:	22.76	47.08	30.16	--
	22.37	47.52	30.11	--
	22.03	47.06	30.91	--
	22.40	47.24	30.36	--
Mean:	22.39(±0.30)	47.23(±0.21)	30.38(±0.37)	

Total % Distribution:

Cl —	CH_2 —	CH_2 —	CH_2 —	COCl
	22.01	46.44	29.87	1.68
RS_5^x	1.00	2.11	1.36	0.08

DISCUSSION

Tables 20, 21 and 22 show the selectivities for the chlorination of the 1,4-disubstituted butanes studied. The chlorination of 1-chloro-4-fluorobutane was attempted but the products could not be satisfactorily separated by any g.l.c. column used and consequently the results have not been included for discussion.

Table 20 Relative Selectivities for the gas phase chlorination of 1,4-disubstituted butanes

Temperature	RS_4^X
120°c	Cl — CH_3 — CH_2 — CH_2 — CH_2Cl 1.00 1.95 1.95 1.00
115°c	F — CH_2 — CH_2 — CH_2 — CH_2F 1.00 1.34 1.34 1.00
130°c	Cl — CH_2 — CH_2 — CH_2 — CH_2COCl 1.00 2.00 2.06 0.18

Table 21 Relative selectivities for the chlorination of 1,4-disubstituted butanes in non-complexing media at 20°c

SOLVENT	RS_4^X
NEAT	Cl — CH_2 — CH_2 — CH_2 — CH_2 — Cl 1.00 2.42 2.42 1.00
NEAT	F — CH_2 — CH_2 — CH_2 — CH_2 — F 1.00 1.58 1.58 1.00
CARBON TETRA-CHLORIDE	Cl — CH_2 — CH_2 — CH_2 — CH_2 — COCl 1.00 1.40 0.56 0.18

Table 22 Relative selectivities for the chlorination of 1,4-disubstituted butanes in 'complexing' media at 20°c

SOLVENT	RS_4^X									
BENZENE	Cl	—	CH_2	—	CH_2	—	CH_2	—	CH_2	— Cl
			1.00		2.05		2.05		1.00	
BENZENE	F	—	CH_2	—	CH_2	—	CH_2	—	CH_2	— F
			1.00		1.27		1.27		1.00	
BENZENE	Cl	—	CH_2	—	CH_2	—	CH_2	—	CH_2	—COCl
			1.00		2.16		1.51		0.05	
CARBON DISULPHIDE			1.00		2.11		1.36		0.08	

One thing is immediately apparent from these results; the selectivities in the gas phase and 'complexing' media are quite comparable whereas the selectivities in 'non-complexing' media are slightly higher. This can be partly explained by existing theory. In the gas phase the deactivating polar inductive effect should only be effective up to the carbon β from the substituent.

$$X - \overleftarrow{CH_2 - CH_2} - \overrightarrow{CH_2 - CH_2} - X \qquad \text{VIII}$$

In complexing media, the inductive effect is reduced to quite and extent, because the strength of the dipole set-up during the abstraction process is diminished due to electron delocalisation over the complexing solvent molecule (see VI and VI, Part Two). Thus, the inductive effect extends along the chain, but to a much smaller extent than in 'non-complexing' media. In 1-substituted butanes, this leads to similar selectivities in the gas phase and 'complexing' solvents. In 1,4-disubstituted butanes this leads to similar selectivities too.

$$X - \overleftarrow{\cdots\cdots}\ CH_2 - CH_2 - CH_2 - CH_2 - X \qquad \text{IX}$$

VIII and IX depict the influence of the inductive effect in the gas phase, and 'complexing' solvents respectively.

In 'non-complexing' media selectivities in 1,4-disubstituted butanes are higher. Here the inductive effect has been established to be effective all along the carbon chain X.

$$\overrightarrow{\qquad\qquad\qquad\qquad}$$
$$X - CH_2 - CH_2 - CH_2 - CH_2 - X \qquad\qquad X$$
$$\overleftarrow{\qquad\qquad\qquad\qquad}$$

This means that the 1 and 4 positions will be deactivated to some extent by the substituent at the far end of the molecule. This does not happen in the gas phase; indeed the 1 and 4 positions will be activated due to some degree of resonance stabilization. Consequently increased selectivity would be expected in non-complexing media, and this is indeed observed.

Comparing the results for 5-chlorovaleryl chloride with those for 1,4-dichlorobutane the competitive inductive effects of the two substituents can be seen. In 'non-complexing' media where the inductive effect is effective all along the carbon chain, the acid chloride seems to be more deactivating than the chlorine substituent. In 'complexing' media, the deactivation is not nearly so marked, but this can again be rationalised by the fact that the inductive effects are partially diminished. The gas phase results indicate that the substituents do not appreciably affect each other beyond their respective β positions.

Considering the gas phase data more closely, the results do seem to be slightly anomalous to existing theory. Table 23 compares gas phase data for 1-substituted butanes and 1,4-disubstituted butanes.

Table 23 Comparison of relative selectivities of 1-substituted butanes and 1,4-disubstituted butanes for gas phase chlorination

TEMP°C	X — CH_2 — CH_2 — CH_2 — CH_2 — Y					REFERENCE
120	Cl -	1.00	1.95	1.95	1.00 - Cl	This work
120	H -	1.54	6.37	2.91	1.00 - Cl	This work
115	F -	1.00	1.34	1.34	1.00 - F	This work
115	H -	1.18	3.23	1.74	1.00 - F	This work
130	Cl -	1.00	2.00	2.06	0.18 - COCl	This work
120	Cl -	1.00	2.91	6.37	1.54 - H	This work
130	H -	1.00	4.08	2.00	0.18 - COCl	45

If it is true that in gas phase chlorination reactions the substituent does not have any effect beyond the β position[23,45] it would be reasonable to expect the β/α rations in 1-substituted butanes to be comparable to those in 1,4-disubstituted butanes. Table 23 clearly shows that this is not the case. In fact, it is only the acid chloride group that has a similar β/α ratio in both cases. When the substituent is chlorine or fluorine, the β/α ratio is less in the 1,4-disubstituted butane than in the 1-substituted butane. It is worth noting that the main evidence for the indictive effect not going beyond the β position in the gas phase comes from experiments on 1-substituted alkanes with acid chloride and acid fluoride the substituents [23,45]. In the light of the evidence here, it may be advisable to re-investigate this effect using other substituted alkanes.

It is possible that the present theory does not wholly explain the directive effects in chlorination reactions. At present, the generally accepted view is that the attack at the α position is mainly governed by the resonance stabilization of the incipient radical by the substituent. It may be that, as well as polar and resonance effects, steric effects are important. However, considerable theoretical calculations will be required to elucidate this.

PART FOUR

The Halogenation of 1-nitrobutane

PART FOUR

The halogenation of 1-nitrobutane

INTRODUCTION

Tedder and co-workers have studied the halogenation of an extensive series of 1-substituted alkanes.[36,41,43,44,45] The effect of both electron withdrawing and electron repelling substituents have been studied. It has been constantly found that only position 1 and 2 are affected in gas phase halogenation. Position 2 is nearly always deactivated due to the polar inductive effect of the substituent. Position 1 is deactivated by electron withdrawing groups and activated to some extent by electron repelling groups. It was decided to extend this study further by investigating the chlorination and bromination of 1-nitrobutane.

The halogenation of nitroalkanes does not seem to have been well studied. Emr[58] attempted the liquid phase chlorination of 1-nitrobutane and estimated the formation of equal amounts of 4-chloro-1-nitrobutane and 3-chloro-1-nitrobutane. This was done before the advent of gas liquid chromatography and consequently requires re-investigation. The liquid phase chlorination of 1-nitropropane using t-butyl hypochlorite was studied by Walling.[40] The results indicate a powerful deactivating effect due to the nitro group. The bromination of nitro alkanes does not appear to have been studied.

EXPERIMENTAL

Materials

Chlorine was used as supplied by British Oxygen Company, Bromine (Hopkin and Williams) was purified by trap to trap distillation before being stored in a large storage bulb.

Solvents were used as supplied by the manufacturers. 1-nitrobutane was prepared by the action of dry silver nitrite on dry 1-bromobutane as described in Vogel.[59]

1-nitrobutane:

n.m.r. δ = 0.8 (triplet, J = 14Hz, 3H, $\underline{CH_3}CH_2CH_2CH_2NO_2$)
δ = 1.2 (sextet, J = 38Hz, 2H, $CH_3\underline{CH_2}CH_2CH_2NO_2$)
δ = 1.8 (pentet, J = 38Hz, 2H, $CH_3CH_2\underline{CH_2}CH_2NO_2$)
δ = 4.2 (triplet, J = 18Hz, 2H, $CH_3CH_2CH_2\underline{CH_2}NO_2$)

APPARATUS AND PROCEDURE

Gas Phase Reactions: Gas phase experiments were carried out on the same static system as described in Part One. The products were collected by the same method described in Part Three.

Liquid Phase Reactions: All reactions in the liquid phase were carried out in the same way as described in Part One.

ANALYSIS OF THE PRODUCTS

The products of all the reactions were analysed by gas liquid chromatography. The same system was used as described in Part One. Only one type of column was used; a 6' glass column packed with 8% 'Apiezon' L on 80/100 mesh 'Chromasorb'.

As only three isomers were formed in any appreciable quantity by chlorinating 1-nitrobutane in the liquid phase, these were separated by preparative g.l.c. and identified by n.m.r.

2-chloro-1-nitrobutane

n.m.r. δ = 1.1 (triplet, J = 16Hz, 3H, $\underline{CH_3}CH_2CH(Cl)CH_2NO_2$)
δ = 1.8 (complex, 2H, $CH_3\underline{CH_2}CH(Cl)CH_2NO_2$)
δ = 4.4-4.6 (complex, 3H, $CH_3CH_2\underline{CH}(Cl)\underline{CH_2}NO_2$)

3-chloro-1-nitrobutane

n.m.r. δ = 1.5 (doublet, J = 7Hz, 3H, $\underline{CH_3}CH(Cl)CH_2CH_2NO_2$)
δ = 2.0-2.6 (complex, 2H, $CH_3CH(Cl)\underline{CH_2}CH_2NO_2$)
δ = 3.9-4.3 (complex, 1H, $CH_3\underline{CH}(Cl)CH_2CH_2NO_2$)
δ = 4.5 (triplet, J = 14Hz, 2H, $CH_3CH(Cl)CH_2\underline{CH_2}NO_2$)

4-chloro-1-nitrobutane

n.m.r. δ = 1.6-2.3 (complex, 4H, $ClCH_2\underline{CH_2}\underline{CH_2}CH_2NO_2$)
δ = 3.6 (triplet, J = 11Hz, 2H, $Cl\underline{CH_2}CH_2CH_2CH_2NO_2$)
δ = 4.4 (triplet, J = 12Hz, 2H, $ClCH_2CH_2CH_2\underline{CH_2}NO_2$)

Preparation of 1-chloro-1-nitrobutane

The sodium salt of 1-nitrobutane was prepared by the reaction of an ethanolic solution of sodium ethoxide with an excess of 1-nitrobutane. Chlorine was then rapidly bubbled into the mixture for about 30sec. The mixture was shaken and analysed by g.l.c., and the existence of a new product was established. The reaction mixture was filtered and the product was separated by preparative g.l.c and identified by n.m.r.

$$CH_3CH_2CH_2CH_2NO_2 + NaOEt \longrightarrow CH_3CH_2CH_2CH\ NO_2^-Na^+ + EtOH$$

$$CH_3CH_2CH_2\dot{C}H\ NO_2Na^+ \xrightarrow{Cl_2} CH_3CH_2CH_2CH(Cl)NO_2 + NaCl$$

1-chloro-1-nitrobutane

n.m.r. δ = 0.9 (triplet, J = 14Hz, 3H, $\underline{CH_3}CH_2CH_2CH(Cl)NO_2$)
δ = 1.2-1.6 (complex, 2H, $CH_3\underline{CH_2}CH_2CH(Cl)NO_2$)
δ = 2.1-2.4 (complex, 2H, $CH_3\underline{CH_2}\underline{CH_2}CH(Cl)NO_2$)
δ = 5.9 (triplet, J = 14Hz, 1H, $CH_3CH_2CH_2\underline{CH}(Cl)NO_2$)

Thus the elution order was established to be in the order:- 1-chloro-1-nitrobutane, 2-chloro-1-nitrobutane 3-chloro-1-nitrobutane and 4-chloro-1-nitrobutane.

Preparation of 1-bromo-1-nitrobutane

The sodium salt of 1-nitrobutane was prepared by reacting an ethanolic solution of sodium ethoxide with an excess of 1-nitrobutane. A small quantity of bromine was added and the mixture shaken for about 30sec. and then filtered. 1-bromo-1-nitrobutane was isolated by preparative g.l.c. using an 8% 'Apiezon L' column on 80/100 mesh 'Chromasorb' at 170°c and then identified by n.m.r.

$$CH_3CH_2CH_2CH_2NO_2 + NaOEt \longrightarrow CH_3CH_2CH_2C\bar{H}\ NO_2Na^+ + EtOH$$

$$CH_3CH_2CH_2\bar{C}H\ NO_2\overset{+}{N}a \xrightarrow{Br_2} CH_3CH_2CH_2CH(Br)NO_2 + NaBr$$

1-bromo-1-nitrobutane

n.m.r. δ = 1.0 (triplet, J = 14Hz, 3H, $\underline{CH_3}CH_2CH_2CH(Br)NO_2$)
δ = 1.4-1.7 (multiplet, 2H, $CH_3\underline{CH_2}CH_2CH(Br)NO_2$)
δ = 2.2-2.6 (multiplet, 2H, $CH_3CH_2\underline{CH_2}CH(Br)NO_2$)
δ = 6.0 (triplet, J = 15Hz, 1H, $CH_3CH_2CH_2\underline{CH}(Br)NO_2$)

The position of the 1-bromo product in a chromatogram was then established. The rest of the products were assumed to elute in the order:-
2-bromo, 3-bromo, and 4-bromo-1-nitrobutane. This is the elution order that has been consistently found for the bromination products of other 1-substituted butanes[60] and consequently it seems safe to make the assumption here.

RESULTS

Gas phase chlorination of 1-nitrobutane over a temperature range

Column: 6' 8% 'Apiezon'L on 80/100 mesh 'Chromasorb' at 150°c

Temperature: 78°c

	CH_3 —	CH_2 —	CH_2 —	CH_2 - NO_2
% Distribution:	26.54	73.46	--	--
	29.57	70.43	--	--
	27.59	72.41	--	--
Mean:	27.90(±1.54)	72.10(±1.54)		
RS_p^s	1.00	3.89(±0.29)		

Temperature: 100°c

	CH_3 —	CH_2 —	CH_2 —	CH_2 - NO_2
% Distribution:	28.82	71.18	--	--
	30.38	69.62	--	--
	29.60(±1.10)	70.40(±1.10)		
RS_p^s	1.00	3.57(±0.18)		

Temperature: 150°c

	CH_3 —	CH_2 —	CH_2 —	CH_2 - NO_2
% Distribution:	29.37	70.63	—	—
	29.38	70.61	—	—
	29.44	70.56	—	—
	29.40(±0.04)	70.60(±0.04)	—	—
RS_p^s	1.00	3.60(±0.01)		

Temperature: 175°c

	CH_3 —	CH_2 —	CH_2 —	CH_2- NO_2
% Distribution:	29.73	70.27	–	–
	30.79	69.21	–	–
	30.58	69.42		
	30.37(±0.56)	69.63(±0.56)	–	–
RS_p^s	1.00	3.42(±0.13)		

Temperature: 200°c

	CH_3 —	CH_2 —	CH_2 —	CH_2 - NO_2
% Distribution:	35.34	64.66	–	–
	34.77	65.23		
	34.09	65.91	–	–
	35.40	64.60		
	34.90(±0.61)	65.10(±0.61)	–	–
RS_p^s	1.00	2.80(±0.08)		

RS_p^s Values for the gas phase chlorination of 1-nitrobutane

Temperature °c	Relative Selectivities			
	CH_3 —	CH_2 —	CH_2 —	CH_2NO_2
78	1.00	3.89	0.00	0.00
100	1.00	3.57	0.00	0.00
150	1.00	3.60	0.00	0.00
175	1.00	3.42	0.00	0.00
200	1.00	2.80	0.00	0.00

Tabulating these results to give Arrhenius parameters:-

$10^3/T$	$\ln(k_3/k_4)$
2.85	0.95
2.68	0.87
2.36	0.88
2.23	0.82
2.11	0.63

Plotting $\ln (k_3/k_4)$ vs $1/T$ gives:-

$E_4 - E_3 = 634(\pm 257)$ cal mol^{-1}

$\ln \frac{(A_3)}{(A_4)} = 0.049(\pm 0.319)$

Liquid phase chlorination of 1-nitrobutane at room temperature

Solvent: Carbon Tetrachloride

$\frac{(SOLVENT)}{(SUBSTRATE)} = 6.60$

	CH_3 —	CH_2 —	CH_2 —	CH_2NO_2
% Distribution:	35.98	55.64	8.38	tr
	36.34	55.61	8.05	tr
	36.79	54.84	8.36	tr
	34.31	55.94	9.75	tr
	36.21	53.95	9.84	tr
	35.93(±0.95)	55.20(±0.81)	8.88(±0.85)	tr
RS_p^S	1.00	2.31(±0.09)	0.37(±0.04)	0.01*

(*this figure was derived by injecting a large quantity of the reaction mixture into a g.l.c. machine and picking up the isomer on the highest sensitivity).

Solvent: Benzene

(SOLVENT) = 7.20
(SUBSTRATE)

	CH_3 —	CH_2 —	CH_2 —	CH_2NO_2
% Distribution:	22.32	71.56	6.12	--
	22.32	70.86	6.82	--
	21.29	72.12	6.59	--
	22.00	71.52	6.48	--
	23.08	70.46	6.46	--
	22.20(±0.65)	71.30(±0.65)	6.50(±0.25)	--
RS_p^s	1.00	4.82(±0.18)	0.44(±0.02)	0.00

The gas phase bromination of 1-nitrobutane

Column: 6' 8% 'Apiezon L' on 80/100 mesh 'Chromasorb' at 180°c
Temperature = 170°c

	CH_3 —	CH_2 —	CH_2 —	CH_2NO_2
% Distribution:	2.38	95.13	tr	2.49
	2.14	95.95	tr	1.91
	1.64	92.57	tr	5.79
	2.08	95.27	tr	2.65
Mean:	2.06(±0.31)	94.73(±1.48)	tr	3.21(±1.75)
RS_p^s	1	70(±10)	--	2(±1)

DISCUSSION

The results for the gas phase chlorination of 1-nitrobutane show that only the 3-chloro and 4-chloro isomers are formed. Consequently, the results obtained over a temperature range only allow the difference in activation energy for hydrogen abstraction for positions 3 and 4 to be calculated. Figure 13 shows the plot of $\ln (k_3/k_4)$ vs $10^3/T$

$$E_4 - E_3 = 634 (\pm 257) \text{ cal mol}^{-1}$$

$$\ln \frac{(A3)}{(A4)} = 0.049(\pm 0.319)$$

Although the results show considerable error, they are quite reasonable considering the small differences in activation energy and the technique used. By assuming that position 3 behaves in the same way as the secondary position in n-butane, the absolute Arrhenius parameters can be determined using the values of Knox and Nelson.[61]

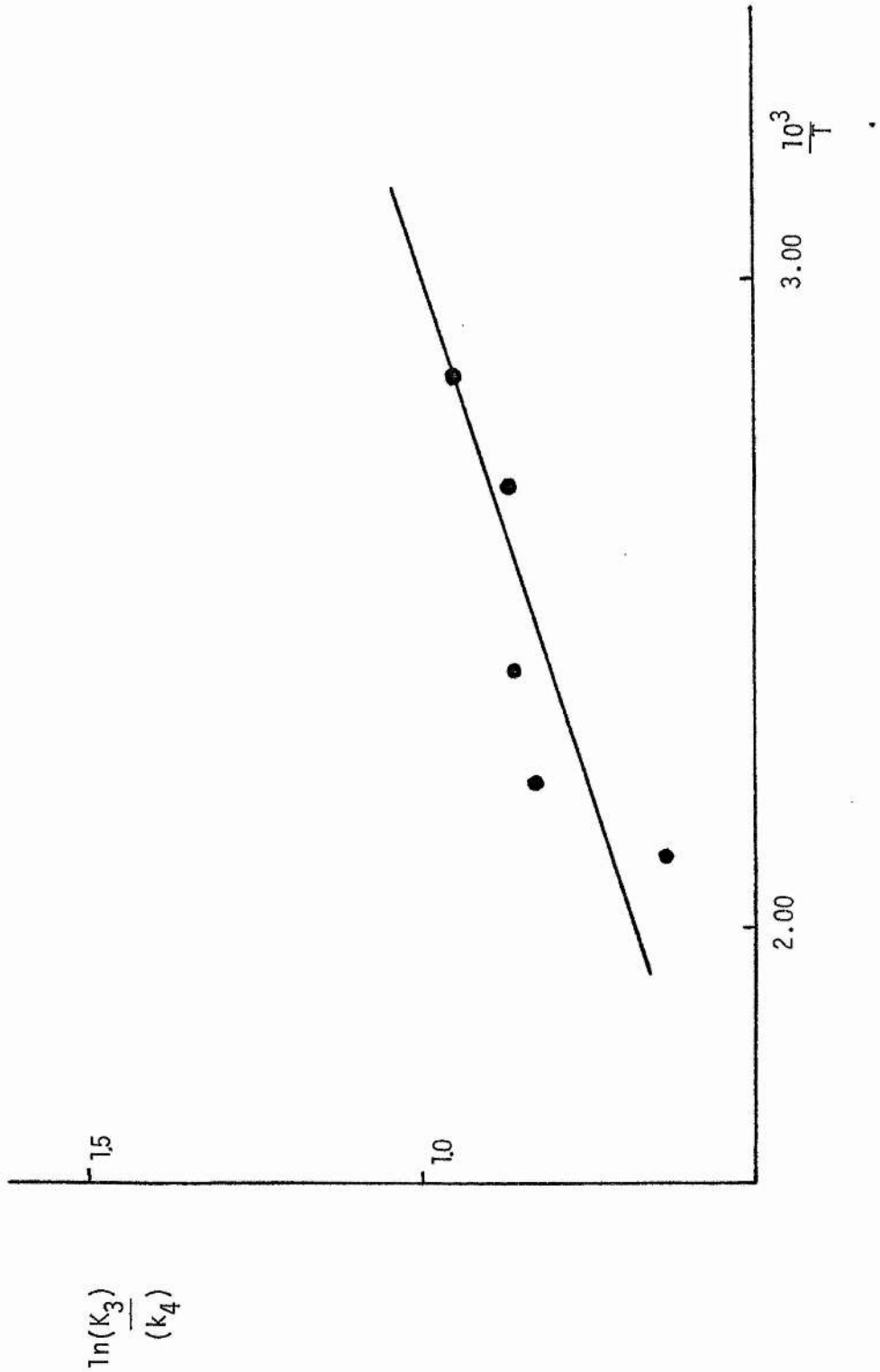
CH_3 — CH_2		— CH_2		— CH_2 — CH_2 - X
E	logA	E	logA	
0.8	13.2	0.3	13.3	-H
0.9	13.2	0.3	13.3	-- -- $-NO_2$

Table 24 compares the results for the gas phase chlorination of 1-nitrobutane with other 1-substituted butanes at 50°c.

Table 24 Relative selectivities RS_4^X for the gas phase chlorination of 1-substituted butanes at 50°c

CH_3 — CH_2 — CH_2 — CH_2 — X	RS_4^X	Ref.
1.00 3.6 3.6 1.0 H		36
1.00 3.8 0 0 $-NO_2$		This work
1.00 4.3 1.2 0.04 $-CF_3$		43
1.00 3.9 1.7 0.2 -CN		44
1.00 3.9 2.1 0.2 -COCl		45
1.00 4.1 2.2 0.8 -Cl		This work

FIGURE 13



CH_3 —	CH_2 —	CH_2 —	CH_2 —	X	Ref.
1.00	3.7	1.7	0.9	$-F$	36
1.00	4.4	0.7	3.5	$-OCH_3$	62
1.00	5.3	2.7	2.9	$-CMe_3$	63
1.00	3.6	1.1	4.4	$-CH=CH_2$	64
1.00	--	1.0	6.5	$-C_6H_6$	65

The results show that of all the substituents studied so far the nitro group is by far the most deactivating. The inductive effect is so strong that no attack could be detected at positions 1 and 2. The selectivity at position 3 is well in line with other results. It adds more weight to Tedder's theory that the inductive effect is not felt beyond the β position in gas phase halogenation of 1-substituted butanes.

Table 25 shows the results of the liquid phase chlorination of 1-nitrobutane.

Table 25 Relative selectivities for the liquid phase chlorination of 1-nitrobutane

SOLVENT	(SOLVENT)/(SUBSTRATE)	RS_4^X			
		CH_3	CH_2	CH_2	CH_2NO_2
CARBON TETRACHLORIDE	6.60	1.00	2.31	0.37	0.01
BENZENE	7.20	1.00	4.82	0.44	0.00

These results are consistent with the results for the liquid phase chlorination of other 1-substituted butanes (Tables 14 and 15 Part Two). The reaction in 'non-complexing' media is much less selective than in the gas phase as would be expected (see Part Two). Attack at positions 1 and 2 can be detected mainly because larger amounts of reaction product were available for g.l.c. analysis.

When the chlorination is carried out in 'complexing' medium the reaction is more selective, with much more attack at position 3. Again, this is consistent with the results for liquid phase chlorination of other 1-substituted butanes in complexing solvents (Table 15 and 16, Part Two).

Table 26 compares the result for gas phase bromination of 1-nitrobutane with those for other 1-substituted butanes.

Table 26 Relative selectivities RS_4^X for the bromination of 1-substituted butanes at 170°c in the gas phase

CH_3 --	CH_2 --	CH_2 --	CH_2 --	X	Reference
1	80	80	1	H	36
1	70	0	2	NO_2	This work
1	80	7	1	CF_3	43
1	80	8	20	CN	44
1	90	7	9	F	36,43
1	80	32	34	Cl	36
1	80	30	30	COCl	45

Because of the endothermic nature of the reaction the degree of bond breaking in the transition state in bromination is much greater than in chlorination. Bromination involves a late transition state i.e. the new radical is almost completely formed, and so resonance stabilization of the incipient radical is much more important than in chlorination. Table 26 shows that in nearly all cases the α position is activated to attack by the bromine atom. The exception is when the substituent is $-CF_3$ and in this case no resonance stabilisation of the α radical is possible anyway. The attack at the α position in 1-nitrobutane, albeit small, is noticeable. The resonance stabilized α radical may be depicted:-

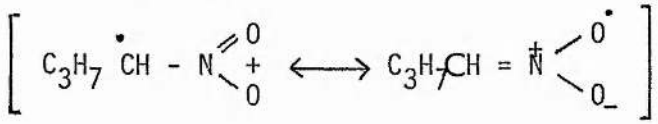


Table 26 also shows that in all cases the β position is deactivated to attack by the bromine atom. As with chlorination, the nitro group seems to be the most deactivating substituent investigated so far. The activation expected at the α position because of resonance stabilisation is considerably offset by the very strong polar inductive effect. Attack at the β position, which is governed solely by the polar inductive effect, cannot be detected in the bromination of 1-nitrobutane. This is in excellent agreement with the chlorination results where attack at the β position is also non existent in the gas phase.

Table 26 shows that the selectivities at the γ positions in the 1-substituted butanes studied are very similar. The attack at position 3 in 1-nitrobutane is in reasonable agreement with the other bromination results. This is again consistent with Tedder's theory that the substituent has no effect beyond the β position in gas phase halogenation of 1-substituted butanes.

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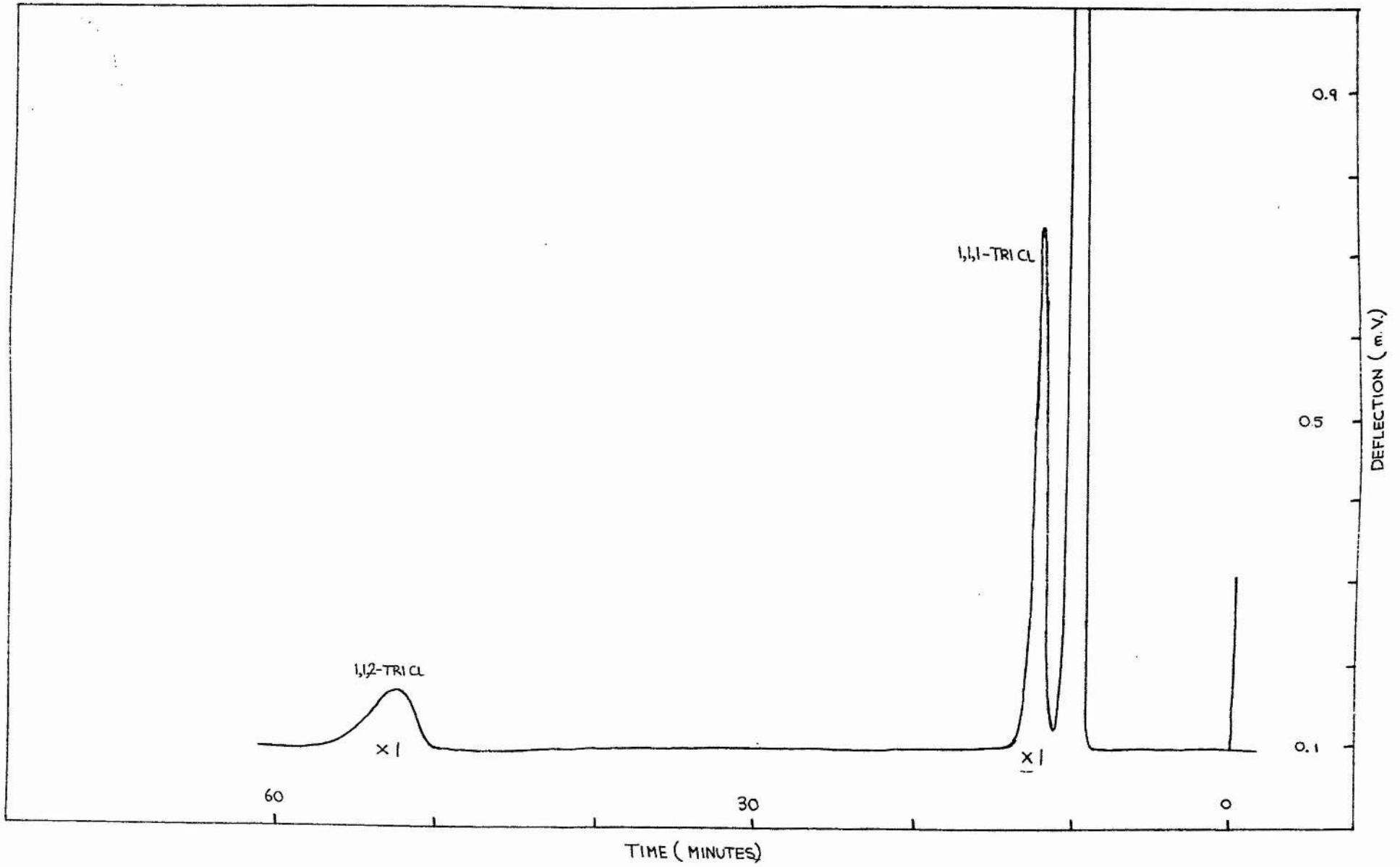
CHROMATOGRAMS

PRODUCTS OF CHLORINATION OF 1,1-DICHLOROETHANE



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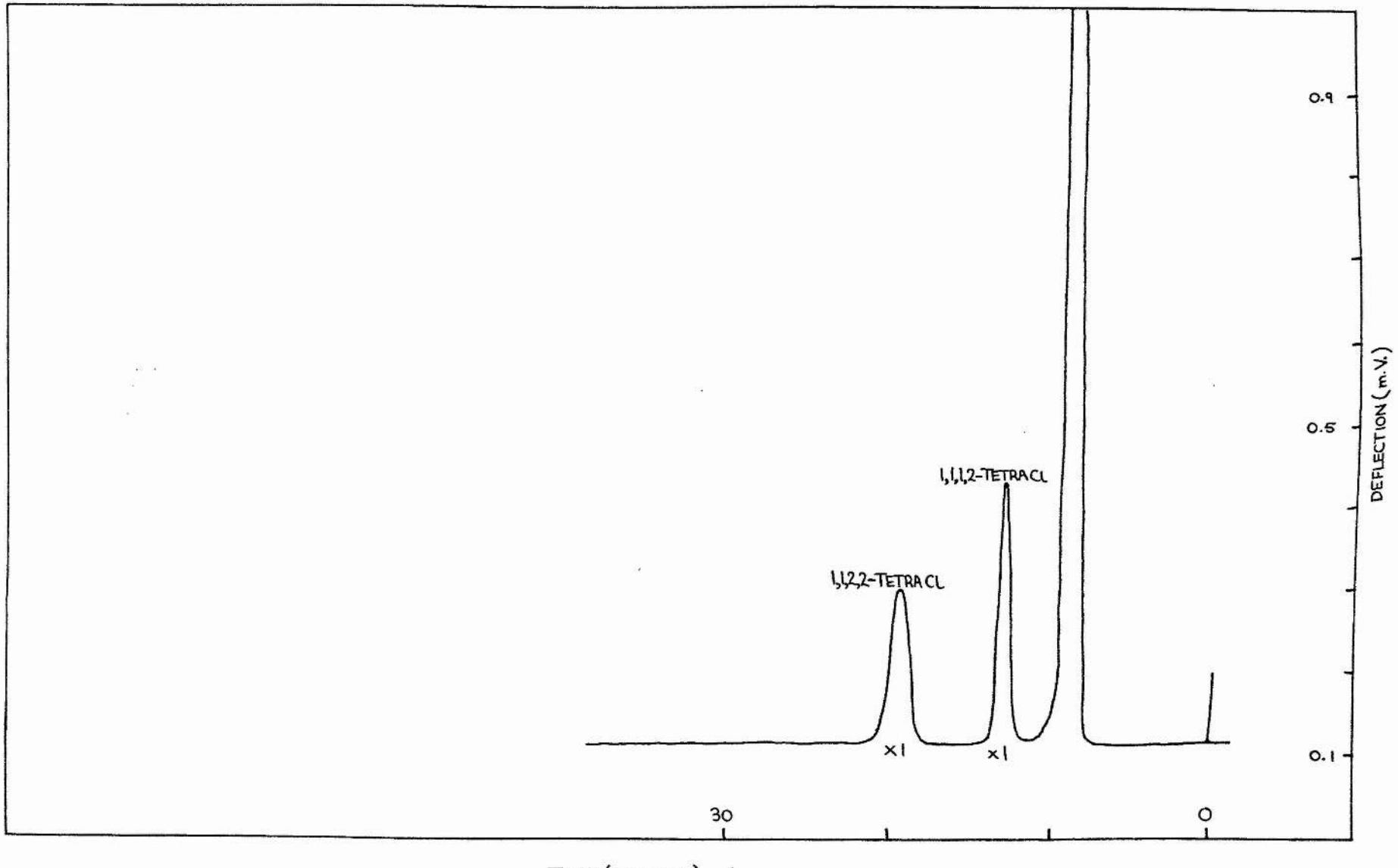

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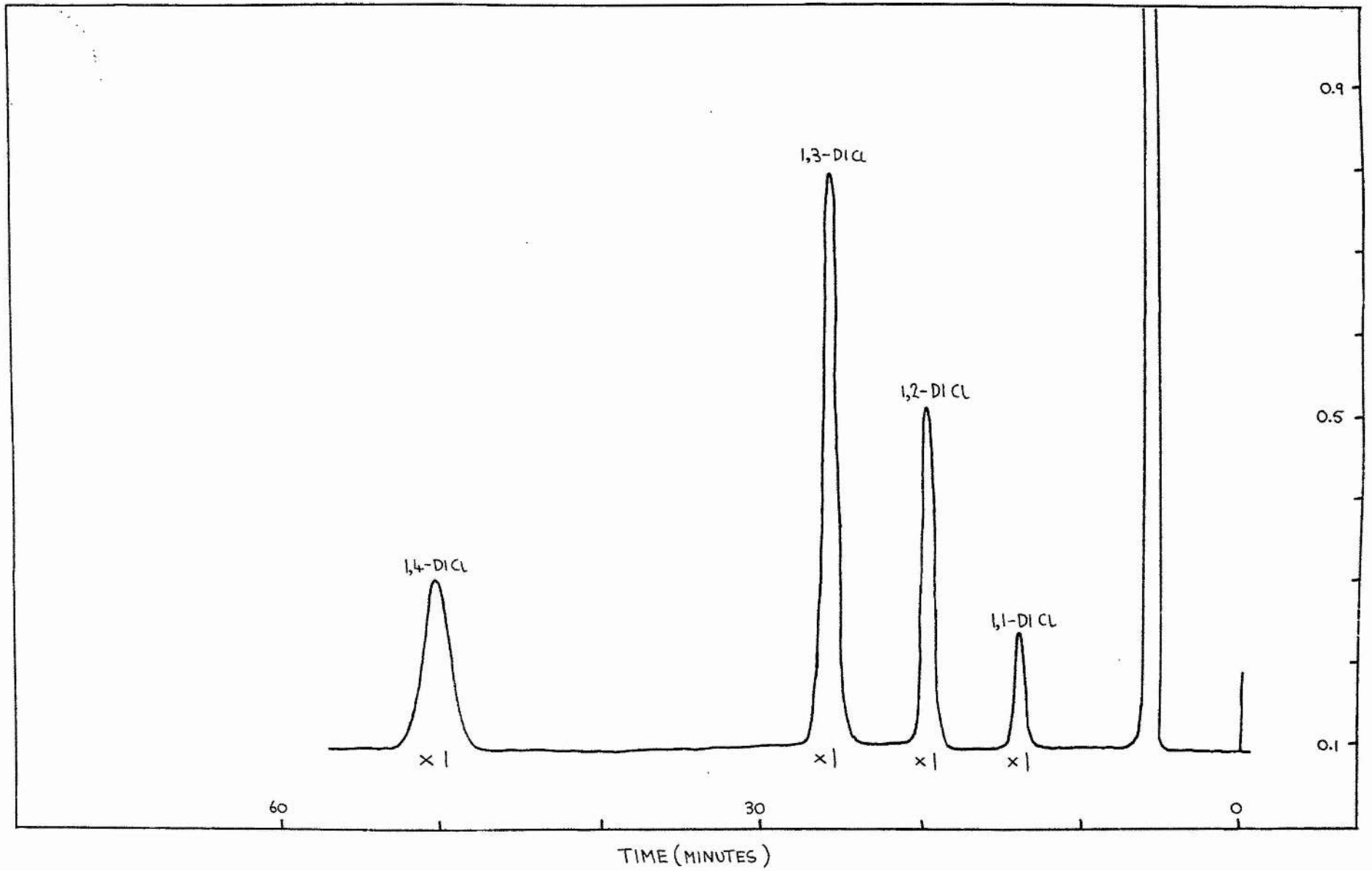

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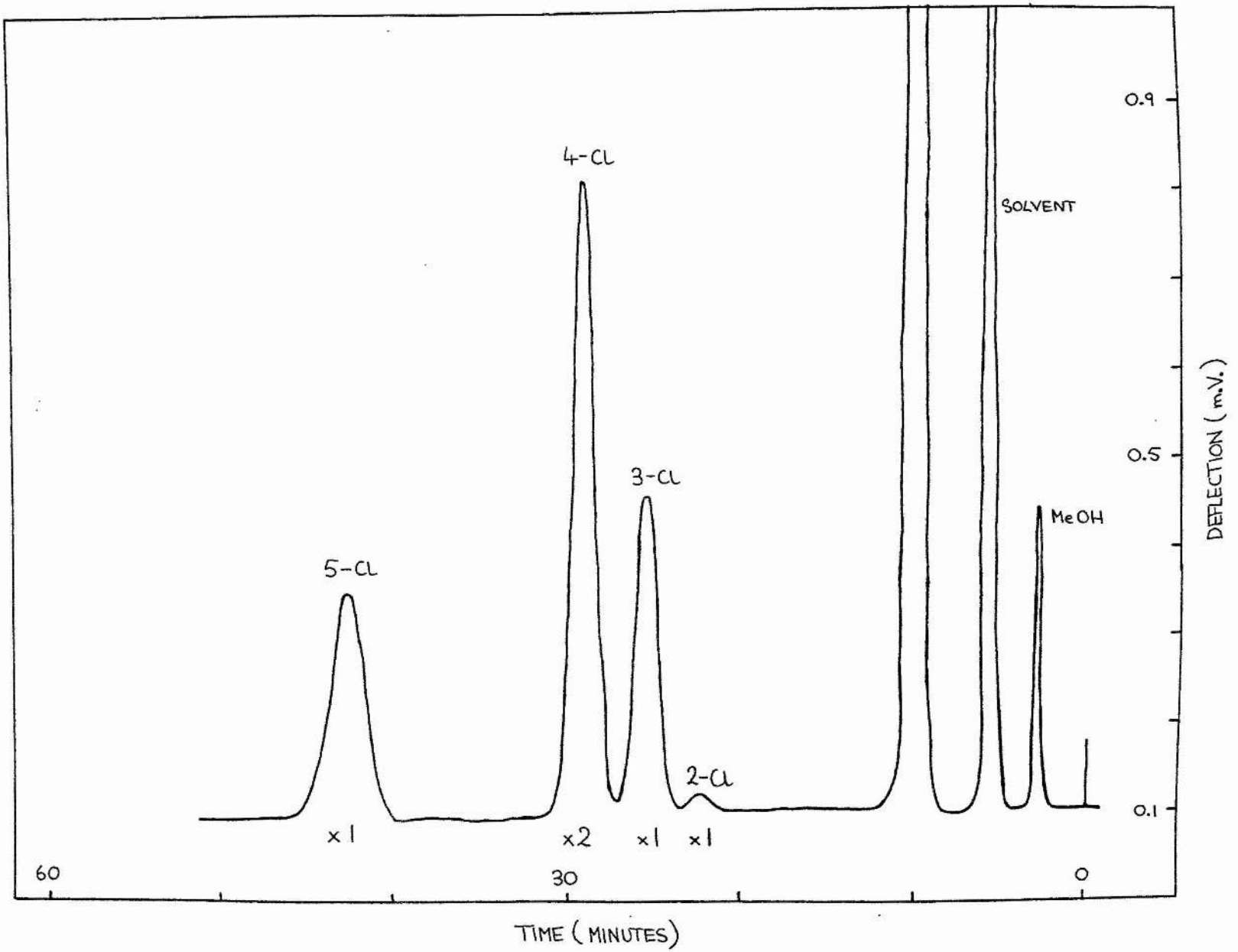

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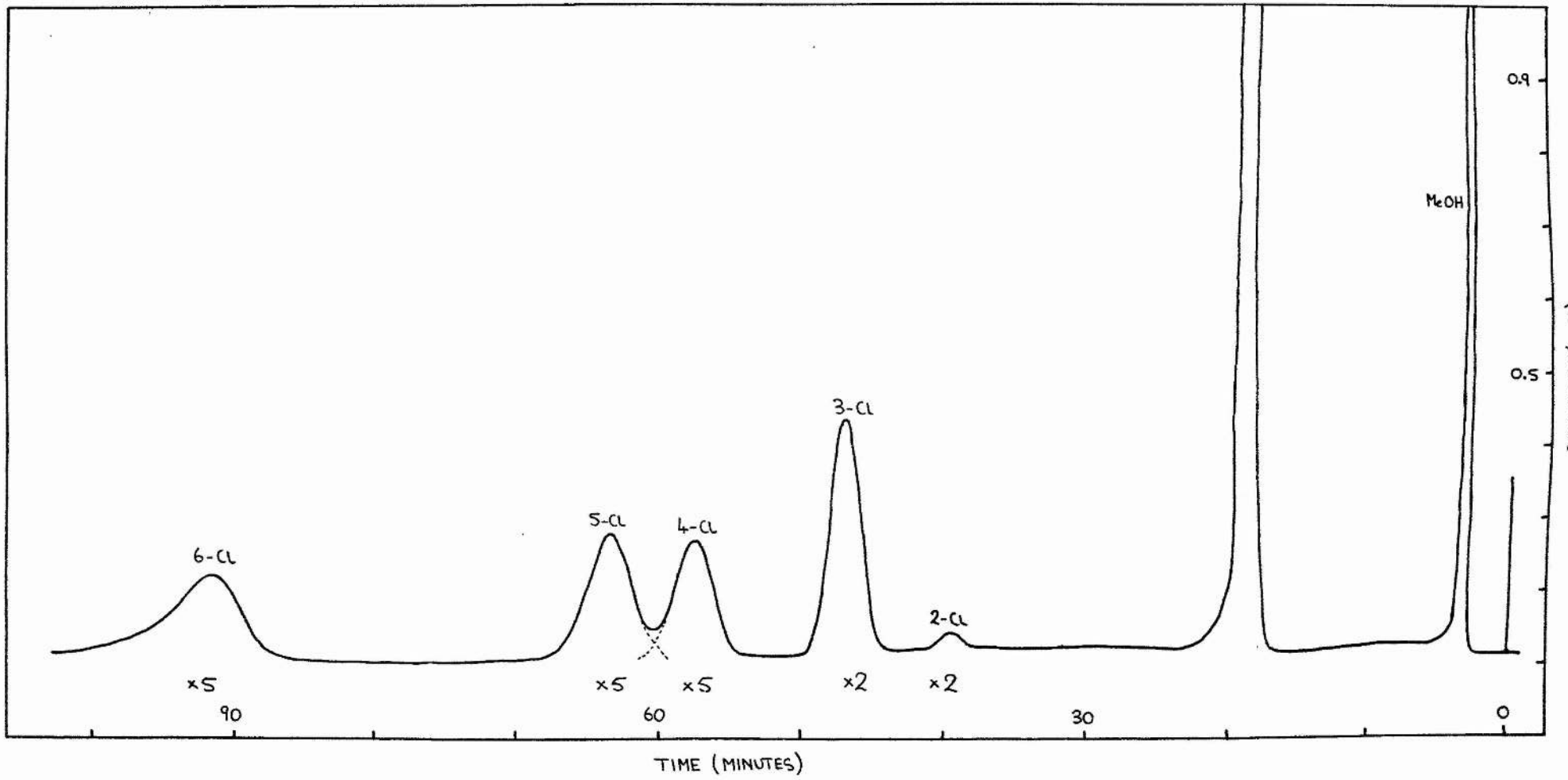

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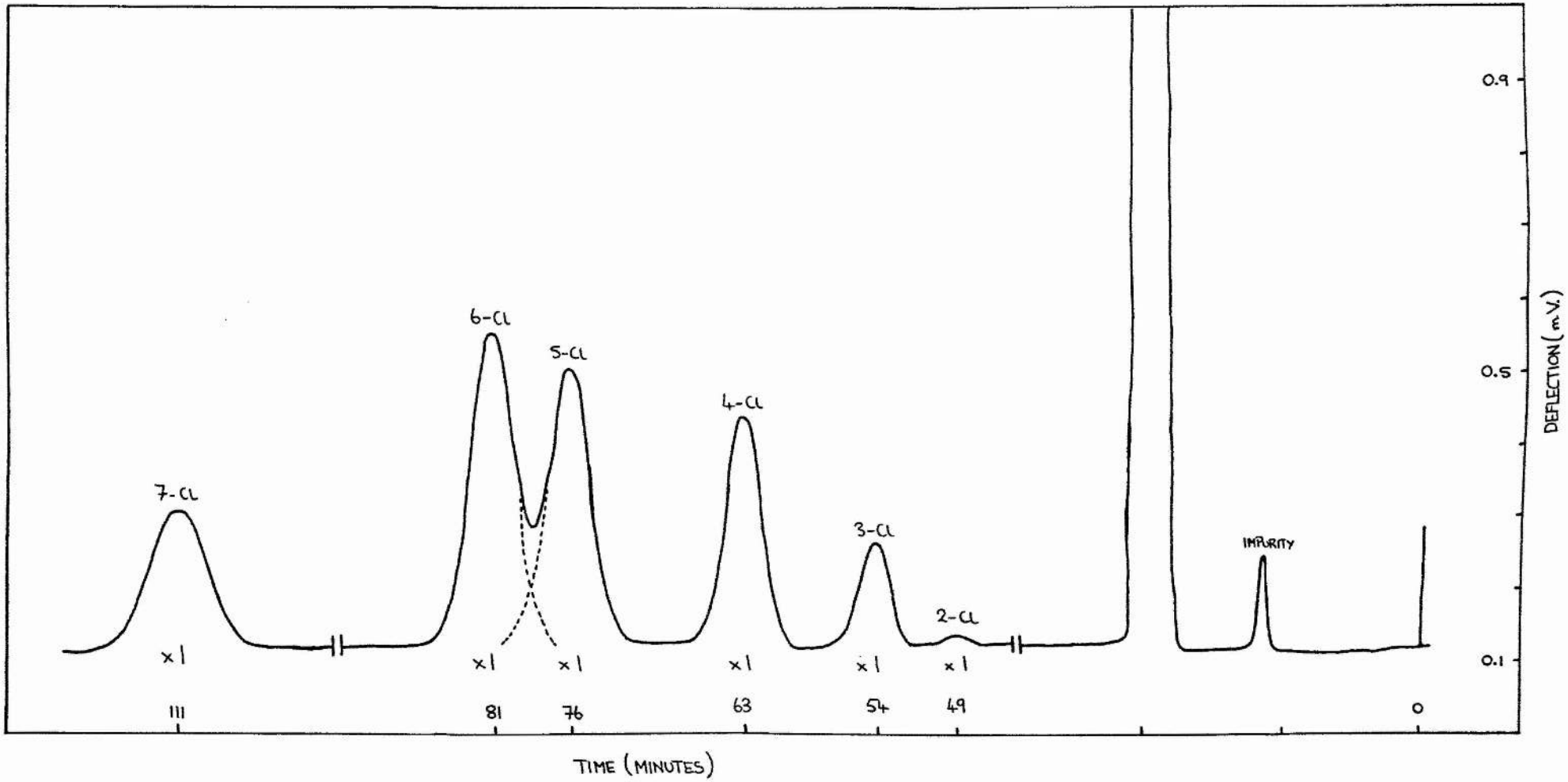
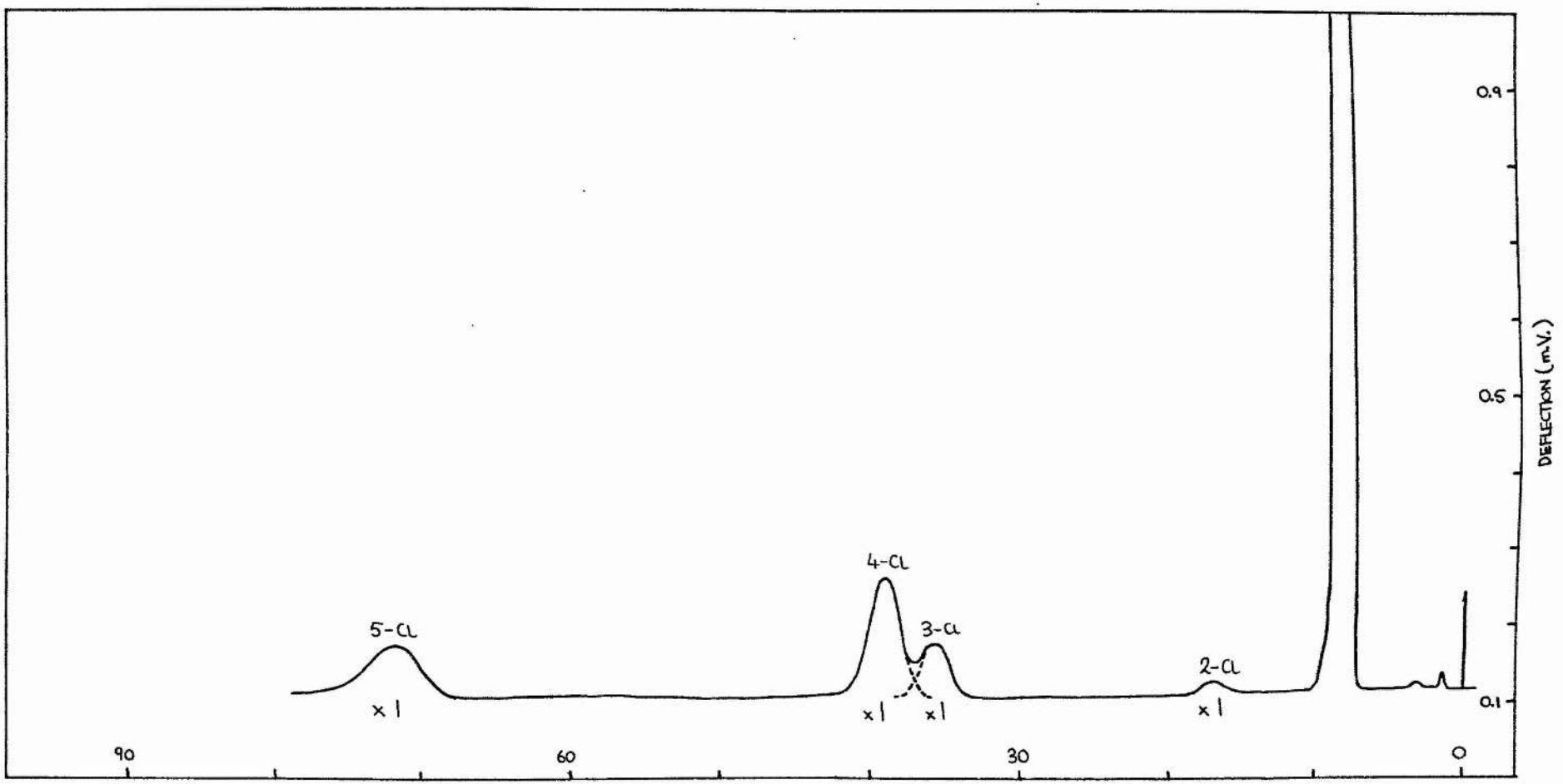
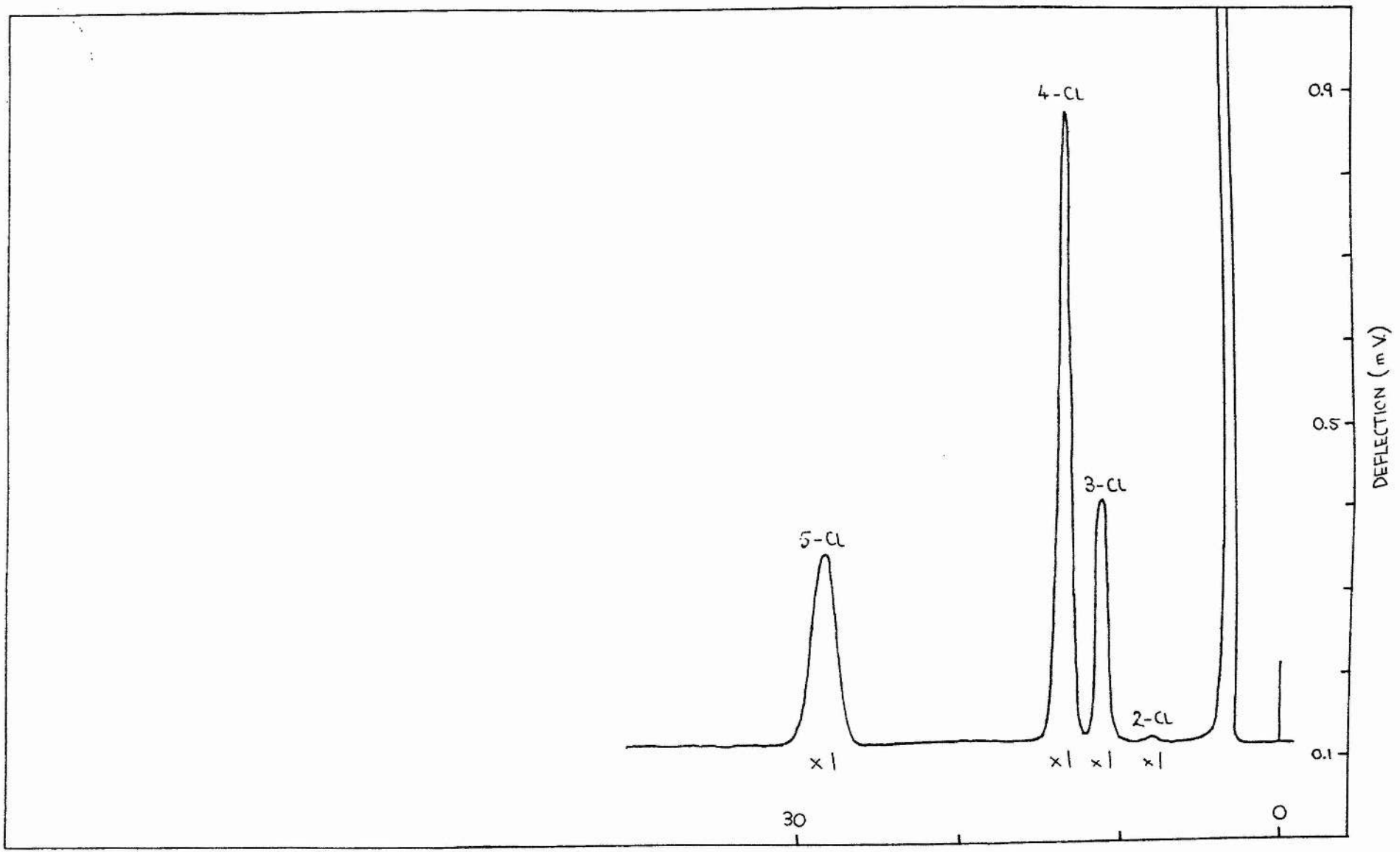


PRODUCTS OF THE CHLORINATION OF VALERONITRILE



PRODUCTS OF THE CHLORINATION OF 1,1,1-TRIFLUOROPENTANE



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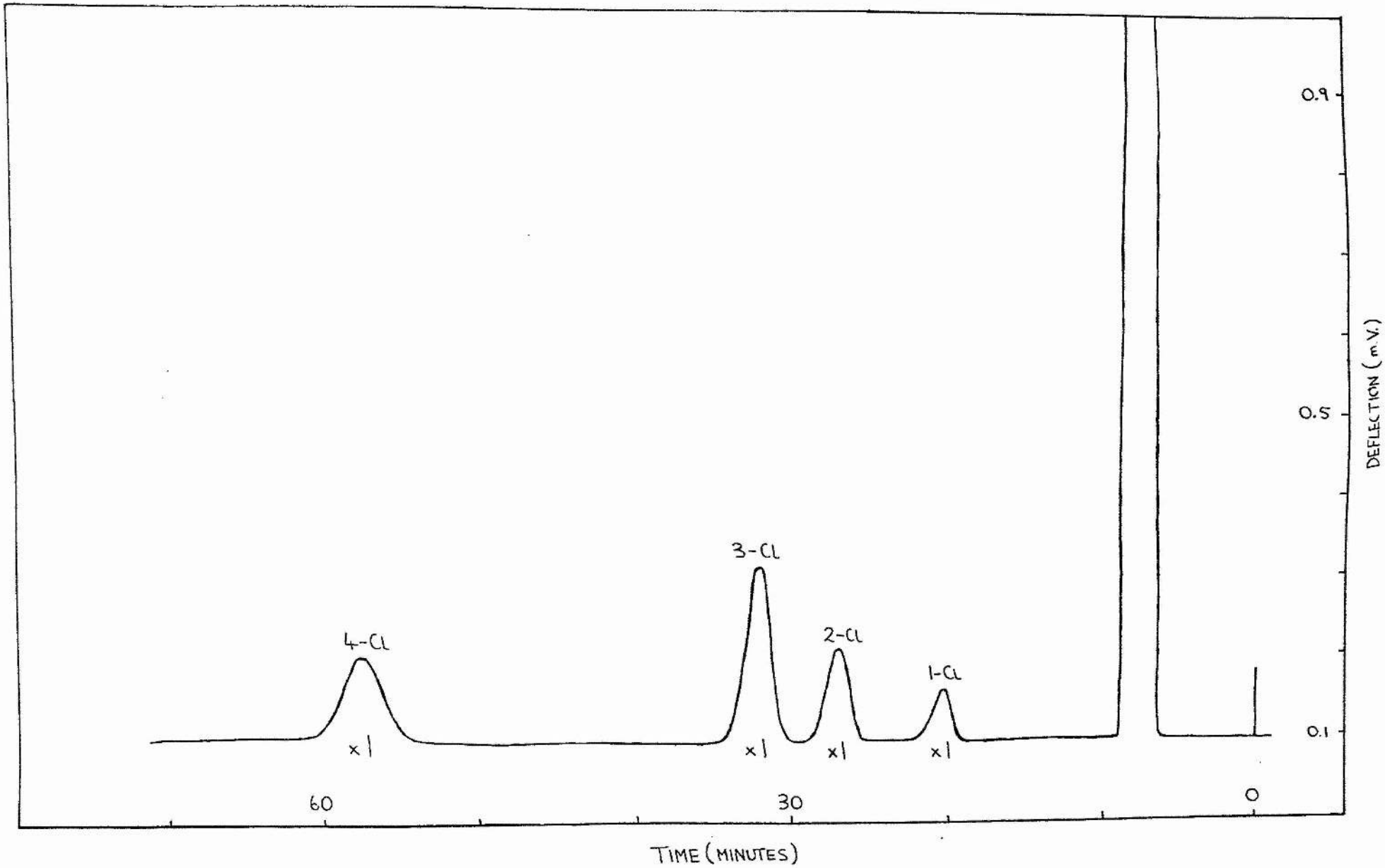

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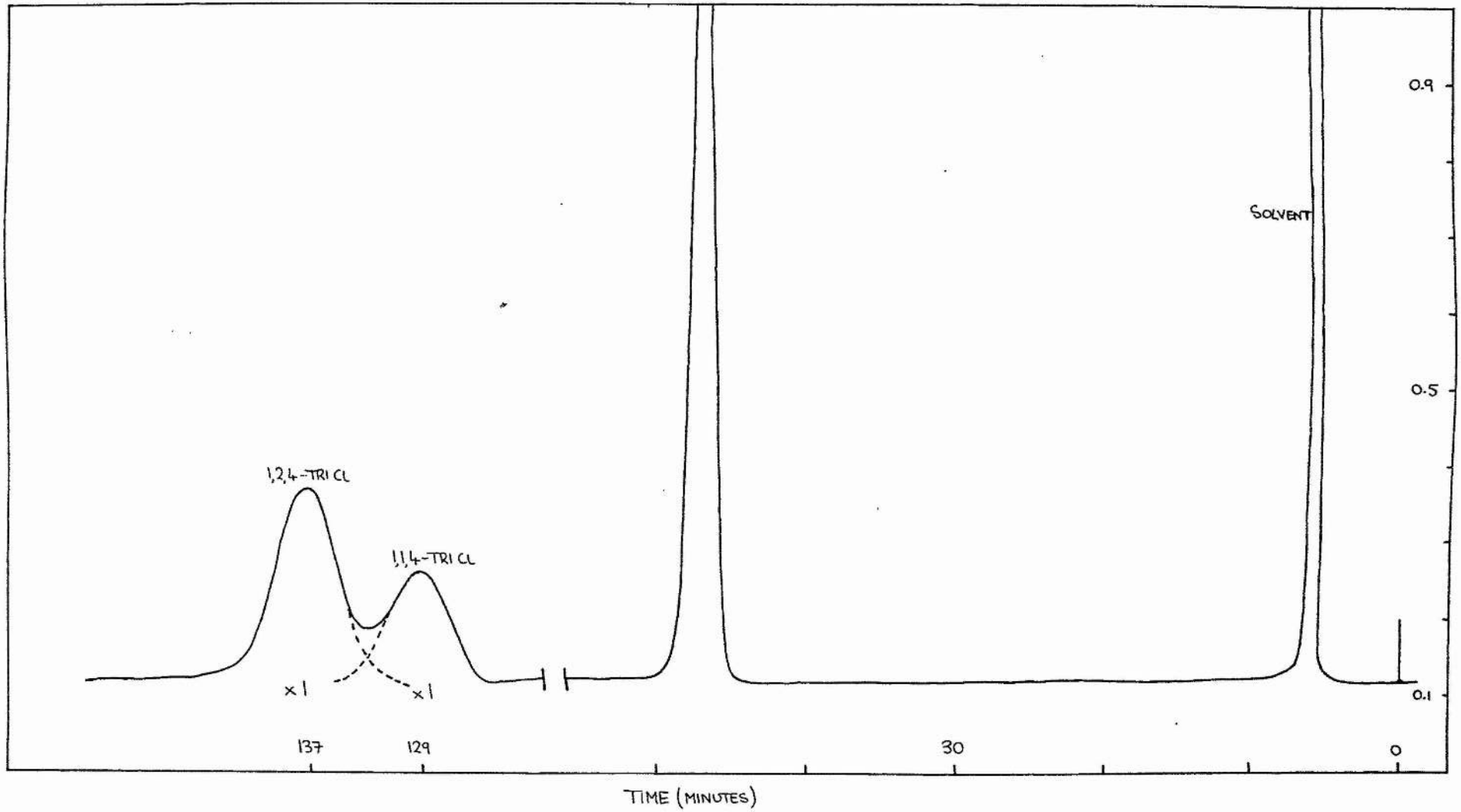

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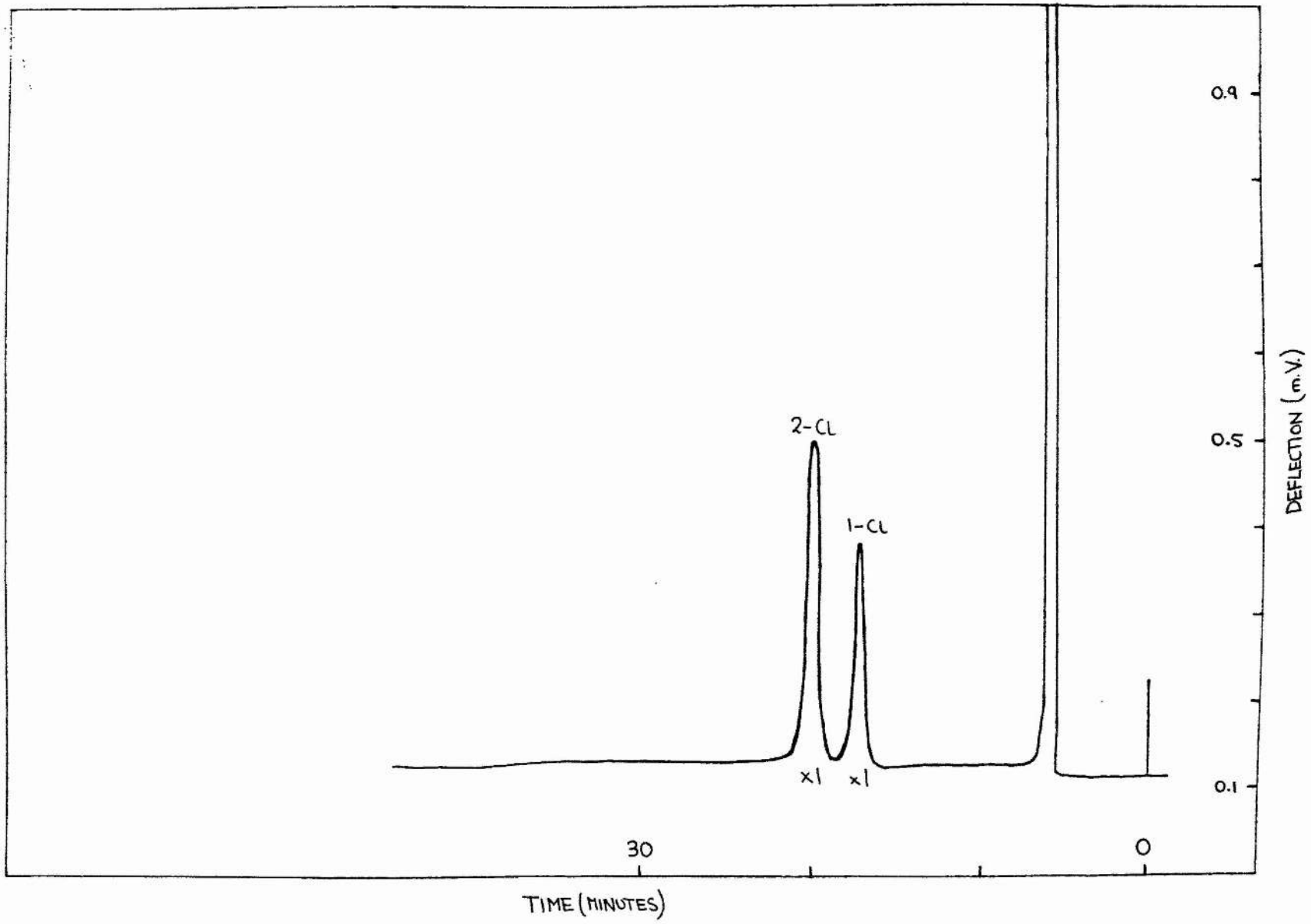

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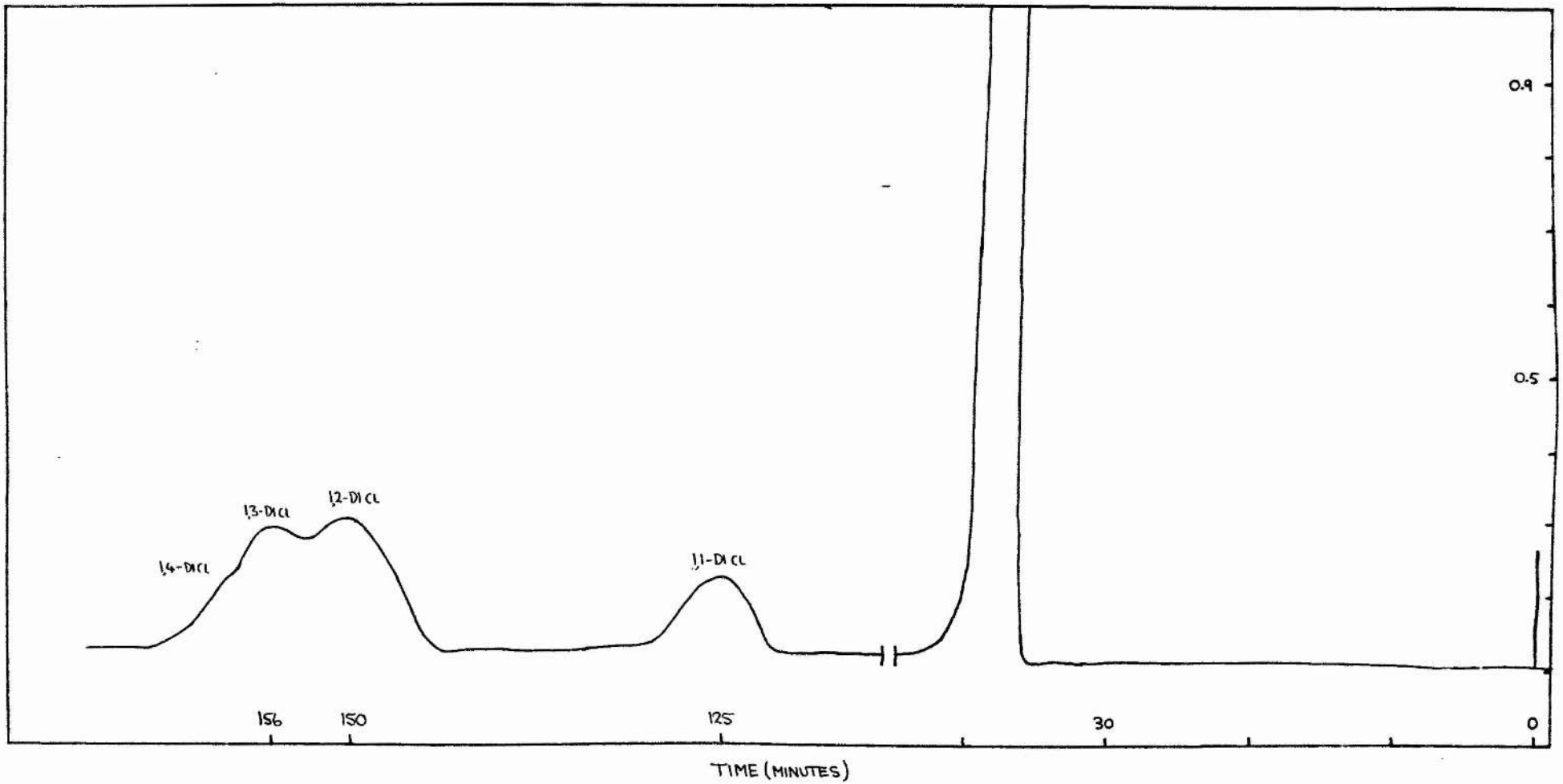

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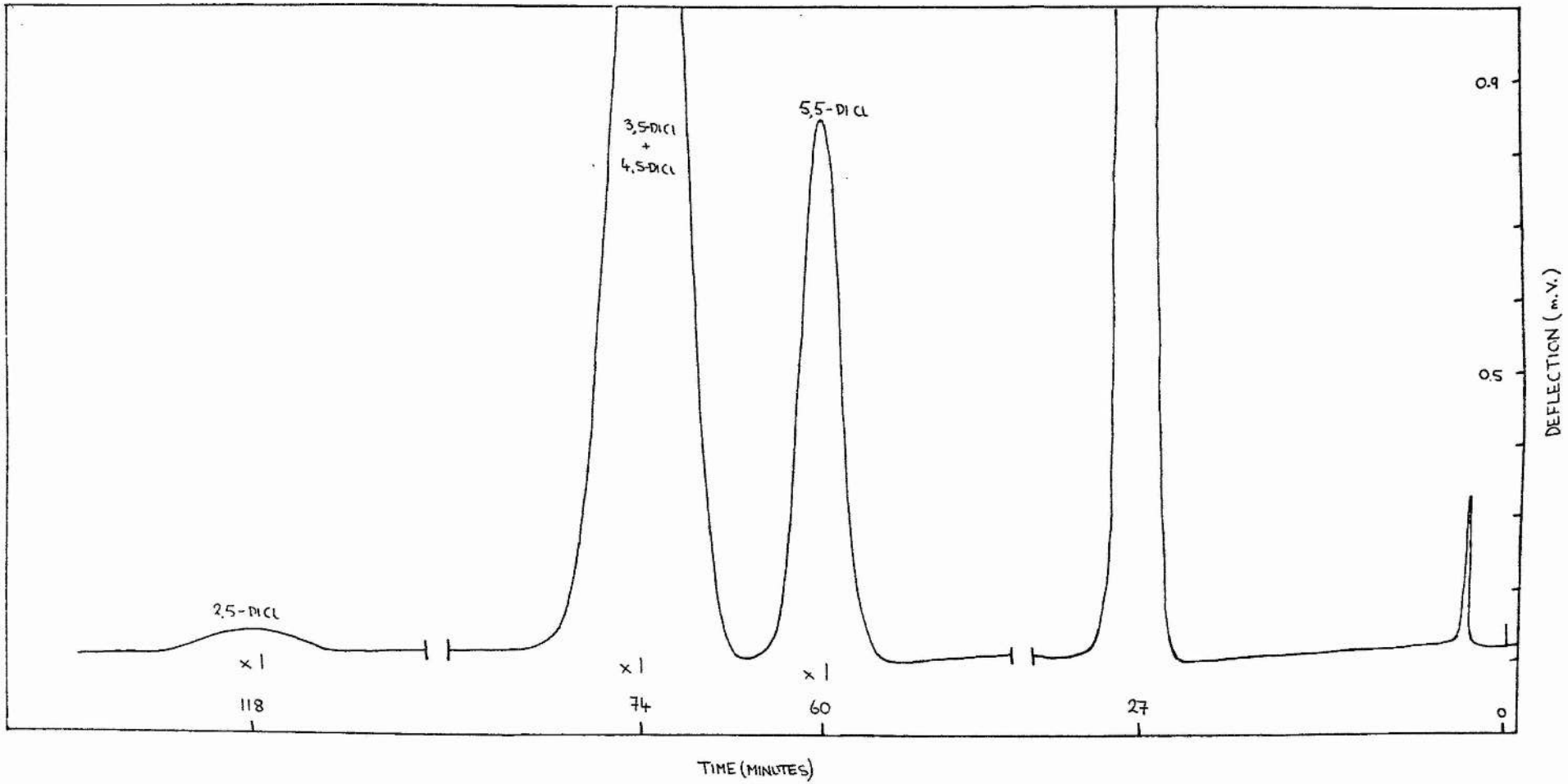

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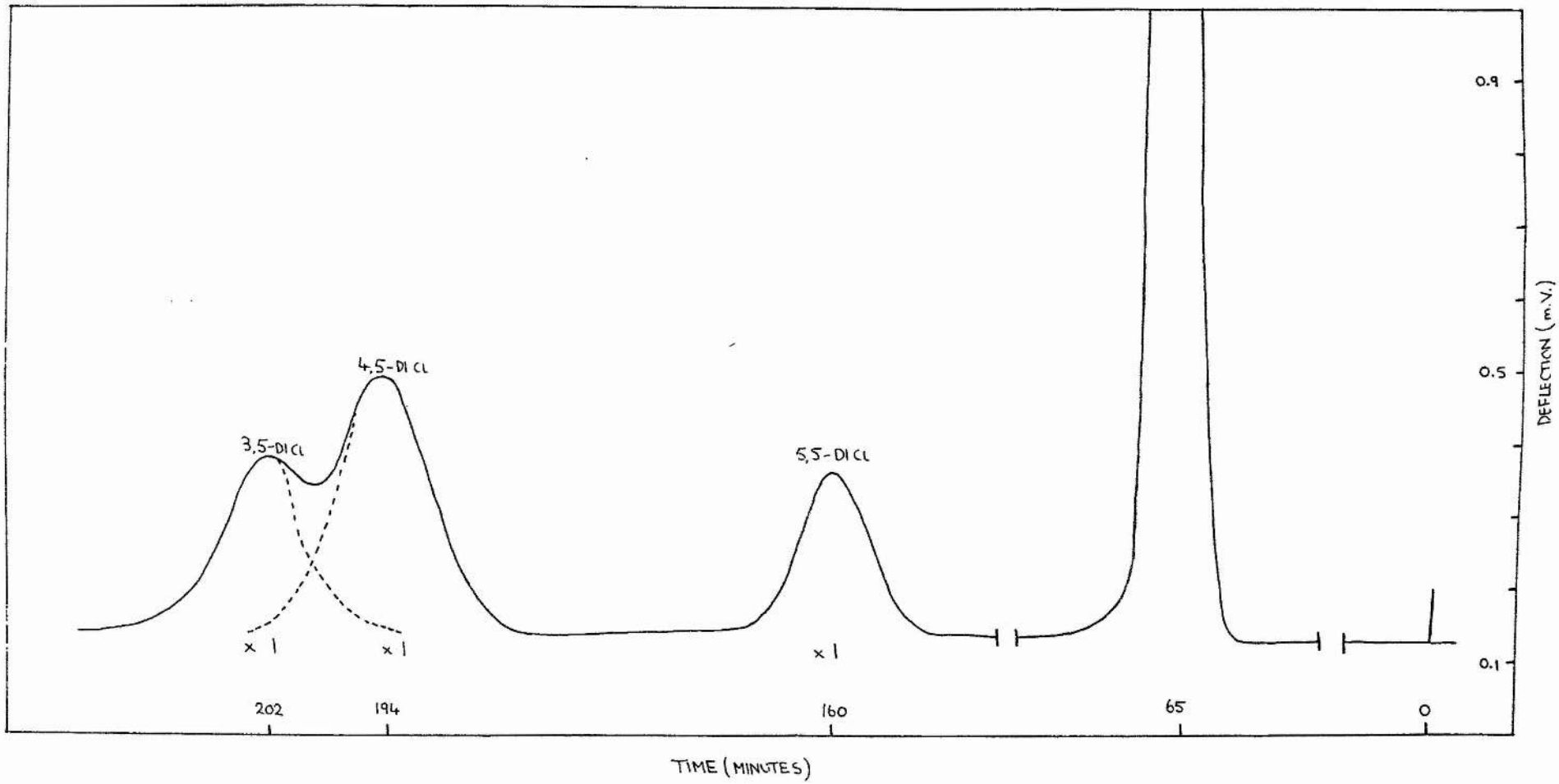

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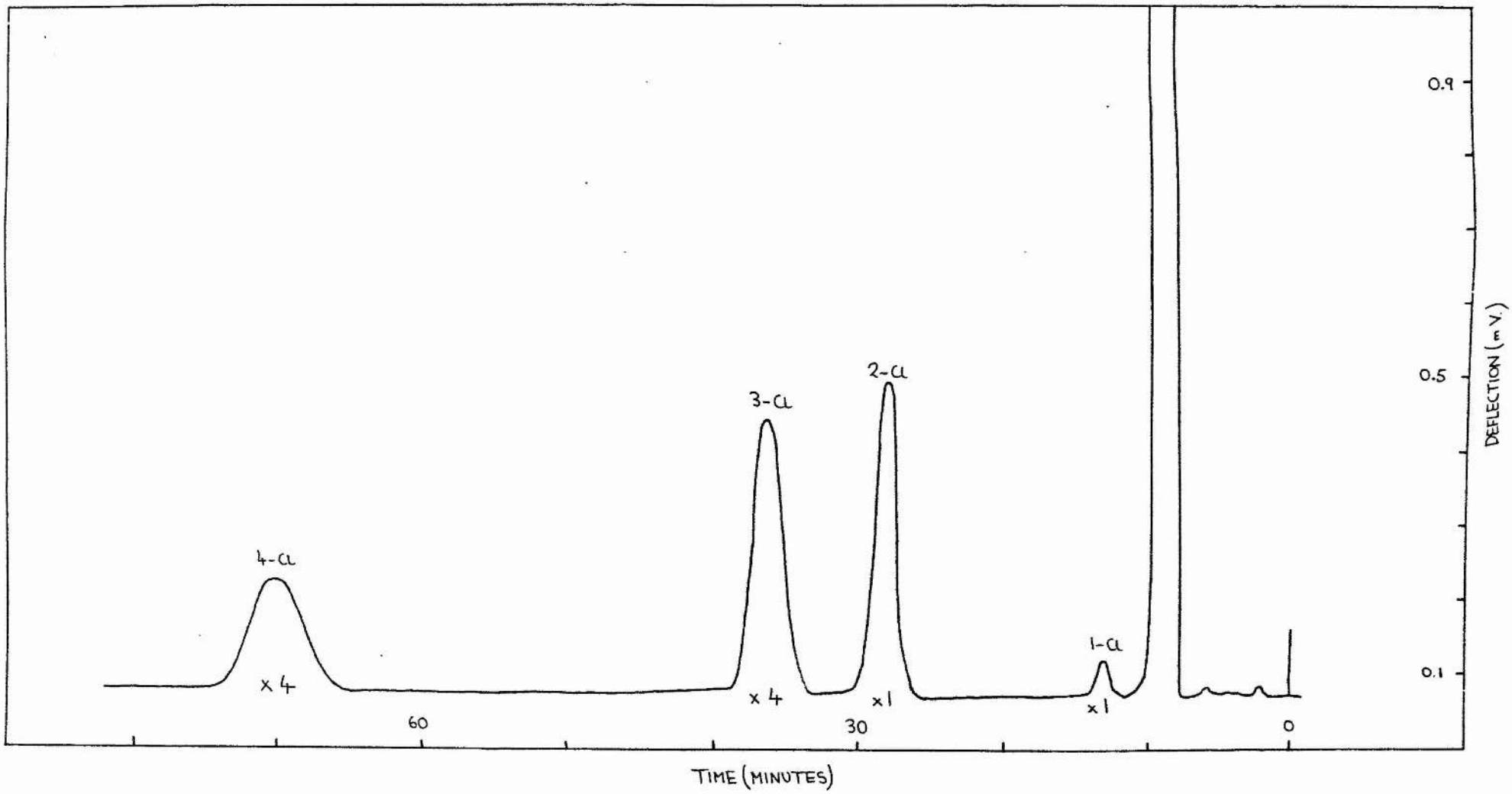

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